JOHN G. McMULLIN

JOURNAL OF

Metals

TECHNOLOGY · PRACTICE

AUGUST 1949

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Fall Meeting Papers

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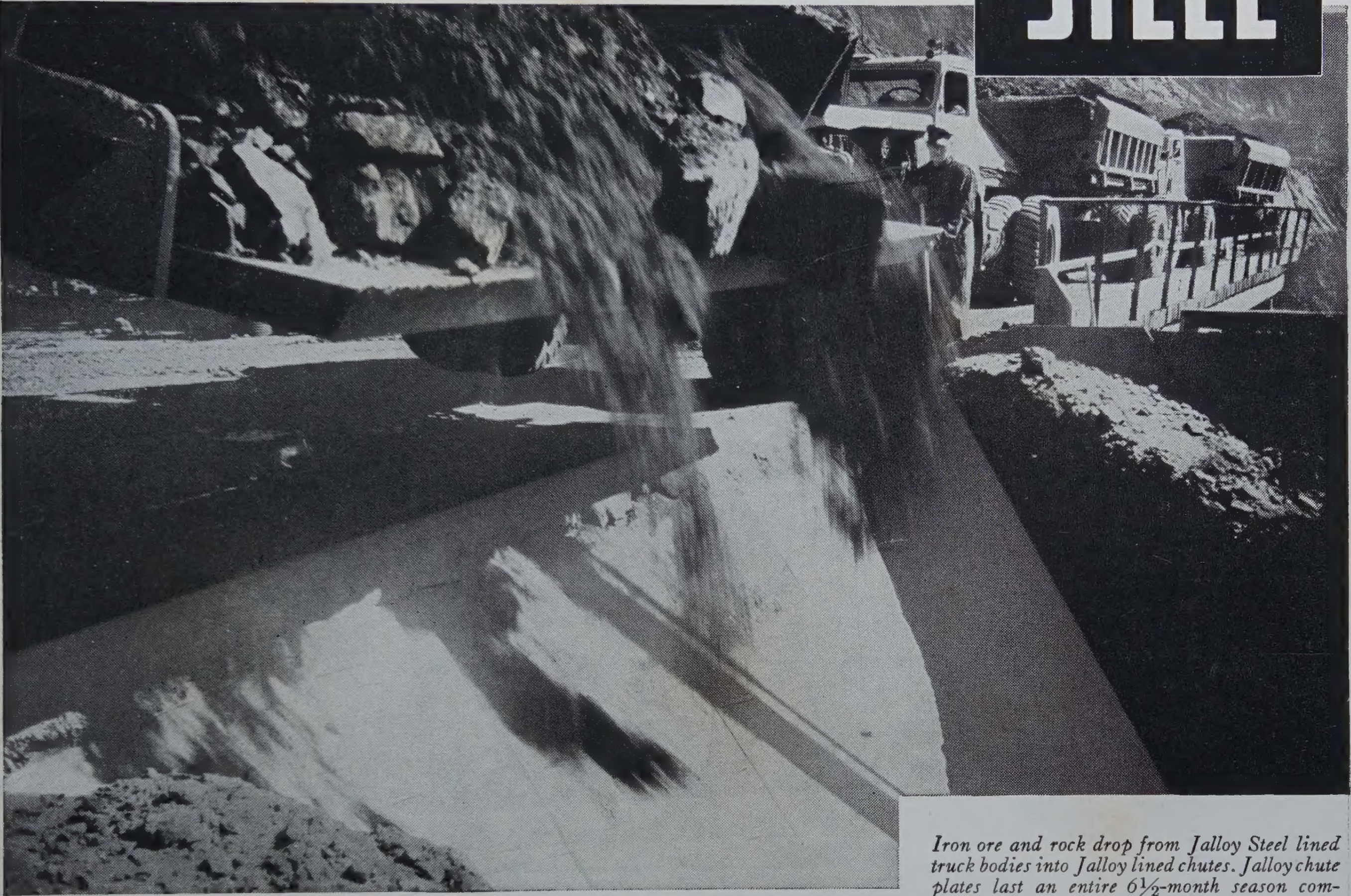

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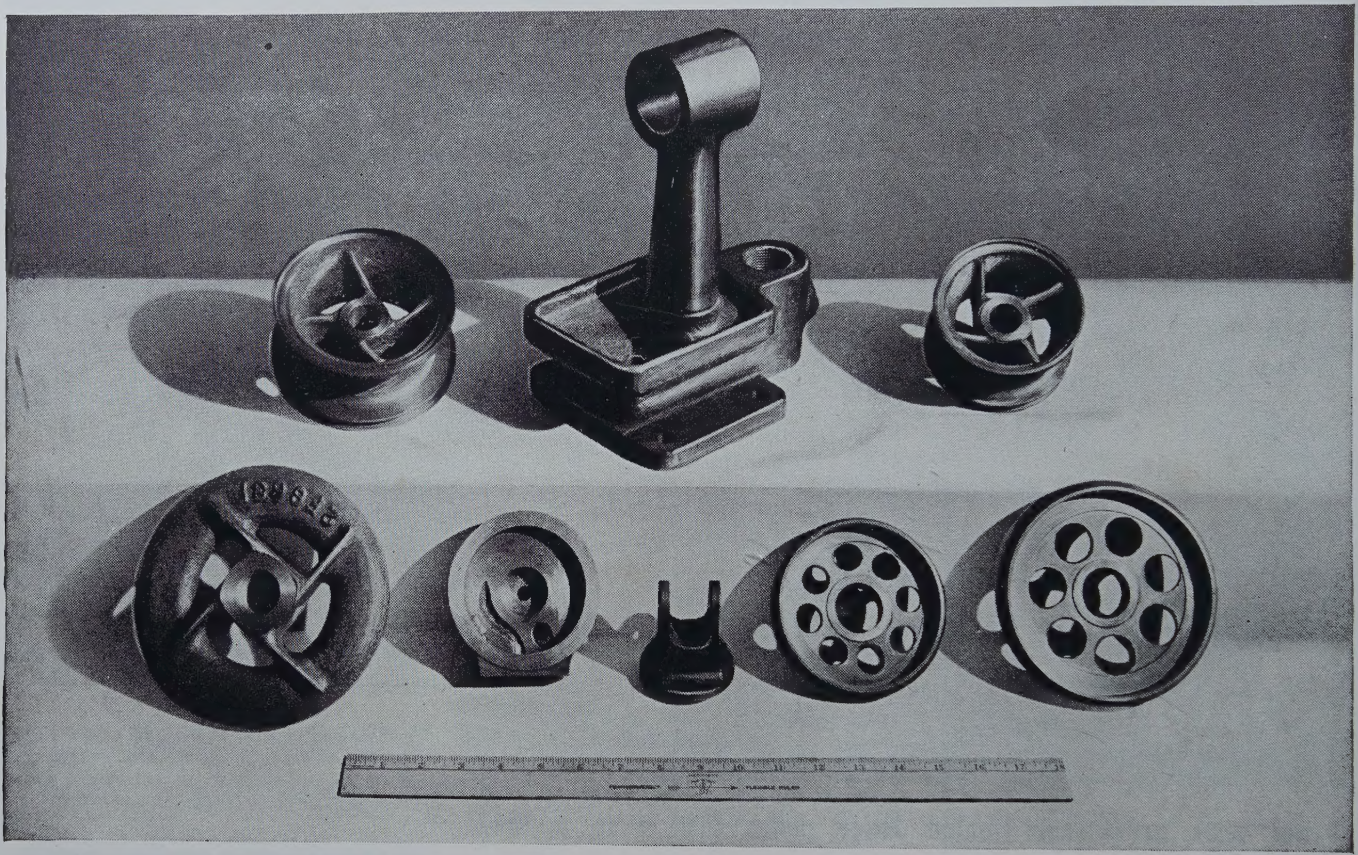

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August 1949 Vol. 1, No. 8

COVER: Charging hot metal into the openhearth — perhaps not the way you see it, but rather through the eyes of that artist with the fantastic ideas of steel making, Boris Artzybasheff. (Courtesy Wickwire Spencer Steel Div.)

section one

EDITORIAL: The Freedom of the Market Place — Felix E. Wormser 5
Sulphur in Basic Iron and Steel — H. E. Warren, Jr. 6
Additional IMD Committee Men 11
Powder Metallurgy Meeting 11
Tentative Papers, Fall Meeting, IMD 12
Among the Manufacturers 13
New Laboratory of General Refractories Co. 14
Book Reviews and Professional Cards 15
Engineering Societies Personnel Service, Inc.
Advertisers' Index Inside back cover

Pages 13-16 in back of book

section two . . . AIME

More Students in Mineral Engineering Courses — W. B. Plank and E. Martinez 249
Board of Directors' Meeting 253
Mid-Year Meeting Plans 254
Drift of Things 255
EJC Questionnaire 256
Calendar of Coming Meetings 256
News of AIME Members 257
Necrology 262
Membership 262

section three . . . metals transactions

EQUILIBRIUM IN THE REACTION OF HYDROGEN WITH OXYGEN IN LIQUID IRON — Minu N. Dastur and John Chipman 441
THE USE OF OXYGEN ENRICHED AIR IN THE METALLURGICAL OPERATIONS OF COMINCO AT TRAIL, B. C. — R. R. McNaughton, T. H. Weldon, J. H. Hargrave, and L. V. Whiton 446
A THERMODYNAMIC INVESTIGATION OF THE SYSTEM SILVER-SILVER SULPHIDE — Terkel Rosenqvist 451
AUTOGENOUS ROASTING OF LOW GRADE ZINC CONCENTRATE IN MULTIPLE HEARTH FURNACES AT RISDON, TASMANIA — J. A. B. Forster 461
EL PASO SLAG TREATMENT PLANT — T. J. Woodside 472
ELECTRICAL RESISTIVITY MEASUREMENTS ON IRON-SILICON COMPACTS PREPARED BY THE POWDER METALLURGY PROCEDURE — Frank W. Glaser 475
A METALLOGRAPHIC DESCRIPTION OF FRACTURE IN IMPACT SPECIMENS OF A STRUCTURAL STEEL — M. Baeyertz, W. F. Craig, Jr., and E. S. Bumps 481
RECOVERY AND RECRYSTALLIZATION IN BRASS — B. L. Averbach 491
FERROMAGNETIC ALLOYS IN THE SYSTEMS Cu-Mn-In and Cu-Mn-Ga — F. A. Hames and D. S. Eppelsheimer 495
SECONDARY RECRYSTALLIZATION IN COPPER — M. L. Kronberg and F. H. Wilson 501
KINETICS OF THE REACTIONS OF ZIRCONIUM WITH O_2, N_2 and H_2. — Earl A. Gulbransen and Kenneth F. Andrew 515
THE ACTIVE SLIP SYSTEMS IN THE SIMPLE AXIAL EXTENSION OF SINGLE CRYSTALLINE ALPHA BRASS — Robert Maddin, C. H. Mathewson, and W. R. Hibbard, Jr. 527

(*Continued on Page 4*)

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Contents (continued)

THE EFFECTS OF MOLYBDENUM AND COMMERCIAL RANGES OF PHOSPHORUS ON THE TOUGHNESS OF 0.40 PCT CARBON CHROMIUM STEELS
M. Baeyertz, W. F. Craig, Jr., and J. P. Sheehan 535

THE EFFECT OF QUENCHING ON THE AGE HARDENING OF TWO ALUMINUM ALLOYS R. D. Barer and M. B. Bever 544

Technical Notes

EFFECT OF CARBON AND NITROGEN ON TEMPER BRITTLENESS
D. C. Buffum, L. D. Jaffe, and W. P. Clancy 499

DISCONTINUOUS CRACK PROPAGATION
L. D. Jaffe, E. L. Reed, and H. C. Mann 526

Salesmanship At Its Best

We have been asked by E. H. Robie to write something about the most recent volume of the Seeley W. Mudd Series, a volume which has been given the fearsome and awe-inspiring title "Bergwerk- und Probierbüchlein" and whose authors are Anneliese Sisco (our better half) and Cyril S. Smith.

This volume contains the translations into English of two German sixteenth-century works, which should appeal to all members of AIME who are interested in the history of their profession. The originals are the "Bergbüchlein," the first text on mining geology ever printed in any language, and the "Probierbüchlein," the first printed work dealing with the assaying of ores and metals and thus with any aspect of metallurgy. They are of interest historically and for the character of their subject matter, and also because there is no question that the great Agricola used both of them as source material when he wrote "De Re Metallica." But they are humble works of literature compared with Biringuccio's (1540), Agricola's (1556), and Ercker's (1573) beautiful books.

The translation as it appears in this Mudd Series volume is an excellent one and retains in large measure the flavor of the sixteenth-century originals. We are sure of this—we should be, having lived with it for years, during which time we witnessed the mental and spiritual anguish that accompanied the search for just the right English equivalent of a German mining or metallurgical term that had disappeared from the German language in the more than 400 years since it was used.

We are also certain that the English text is technically correct; Mrs. Sisco could have found no better collaborator on the "Probierbüchlein" than Cyril Stanley Smith, whose translations (with Mrs. Gnudi) of Biringuccio's "Pirotechnia," also published by the Mudd Fund, was a best seller for some years and now is a collector's item. In addition, a number of outstanding experts (named on p. 64) gave their time willingly to assist in clearing up some of the knottier problems on the "Bergbüchlein."

The book is also of interest because it shows how little human nature, especially in the mining field, has changed in 400 years. Witness the following, spoken by young Knappius, the apprentice miner, who was being instructed by Daniel, the expert: "I want to ask this: In what direction or face in the shaft or at what corner of the drift would my . . . share be located?—so that I can see in the pit what profit I can expect." No wonder Daniel replied "Your ignorance about mining has driven me to undertake this job . . . If you value gain more than the art, you will have to do without either art or profit."

Both Mrs. Sisco and Dr. Smith have done a splendid job in putting these little books into clear but flavorsome English, and the Mudd Fund is to be congratulated for underwriting their publication. The format was designed by Carl Purington Rollins and one thousand copies were printed by the Yale University Press; so only one AIME member out of twenty can own this book ($3.00 to AIME members, $5.00 to others.) An early order is indicated.—*Frank T. Sisco.*

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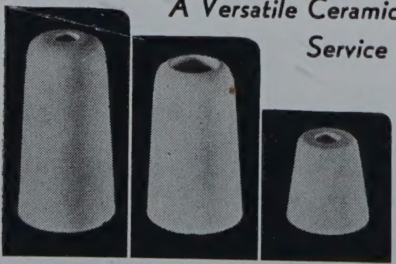

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GUEST EDITORIAL

FELIX E. WORMSER • VICE PRESIDENT, ST. JOSEPH LEAD CO.

THE FREEDOM OF THE MARKET PLACE

If I were asked to define one thing which, above all others, is causing so much economic turmoil in the world, I would reply distrust by government of free markets and its interference with them. No one knows who devised open or free markets—perhaps the greatest "invention" of mankind—but, over hundreds of years, free markets have been an inestimable boon to humanity in directing the energies of the people by signalling when too much of a commodity is being produced and when too little. Prices operating in a free market automatically regulate production and consumption. What a beautifully simple mechanism a free market is, and yet, governments are constantly trying to get away from this simple mechanism and substituting their own limited judgment for that of the market place.

In our own country, and others, a bewildering number of new terms have been coined to describe economic phenomena that either depart from the operation of free markets or obscure old and time-worn principles. Such terms as "dollar shortage," "purchasing power," "government planning," "stabilization," "conservation payments," and others are illustrations. "Dollar shortage" is a new term that nobody emphasized before World War II. It has been introduced because of some government's refusal to allow export and import commerce to progress without government hindrance, which would mean allowing foreign exchange to reach its true level in a free market. No one worries about the balance of payments between the State of New York and other States; it is never given a thought, because we have completely free trade with other states and know that interstate trade will adjust itself automatically.

Take "government planning." Formerly, when government undertook to plan for the citizen for his everyday livelihood, we termed it "socialism." We now use the much more pleasant connotation of "planning," but, lurking in the background is the seemingly innocuous but highly important matter of government compulsion. It is only through the compulsory power of the state that planning can be achieved in accordance with the decrees of the planners, and then only by destroying free markets and having the government take over the marketing function itself. The same comment might do for the pitifully overworked term, "stabilization." We are never told exactly what is to be stabilized, where, and why, and who is to decide.

Now that we are in a recession, we may expect to hear the need for more "purchasing power," though the banks are fairly bursting at the seams with money. Coming closer to home, we find that "conservation payments" and "premiums" are alternate terms for that ugly word, "subsidies." Here, again, government would interfere with the operation of a free market by favoring some producers at the expense of others. Subsidies of any description involve control, and those expecting a hand-out from government without ultimately incurring a price to pay, merely delude themselves. Indeed, it is time for all of us to stop fooling ourselves with designations that conceal their true significance, for if there is one objective common to government all over the world, it is the steady drive for more control—control over every aspect of our lives and, as someone said, "Control, like sin, we first endure, then pity, then embrace."

This leads to a simple conclusion, that one of the highest obligations for all who are freedom-minded, and most Americans are—is to resist government encroachment or interference with our open competitive economy. European economies, with their controls and cartels, have demonstrated conclusively, by contrast, that the American competitive economy is the greatest system ever conceived for the improvement of us all.

I cannot do better than conclude with the philosophy of a great American, General Eisenhower, who had some interesting comments to make recently on individual liberty:

> "Millions of us, today, seem to fear that individual freedom is leading us toward social chaos; that individual opportunity has forever disappeared; that no person can have rightful title to property; that we have reached the point where the individual is far too small to cope with his circumstances; that his lifelong physical security against every risk is all that matters. More than this, we hear that such security must be attained by surrendering to centralized control the management of our society. In short, to these fearful men, the free human individual is a social anachronism.
>
> "On every count the fearful men are wrong. More than ever before, in our country, this is the age of the individual. Endowed with the accumulated knowledge of centuries, armed with all the instruments of modern science, he is still assured personal freedom and wide avenues of expression so that he may win for himself, his family and his country, greater material comfort, ease and happiness; greater spiritual satisfaction and contentment."

Sulphur in Basic Iron and Steel

H. E. WARREN, JR. • Director of Steel Products, Carnegie-Illinois Steel Corp.

From past experience in the Homestead District Works, it had been found that there was no correlation between sulphur in the iron and sulphur in the steel. A study was initiated by Messrs. Philip Schane and Lou Robinson of the Process Control Div. and members of the Metallurgical Dept. to determine the disposition of the sulphur in the iron and to find what factors affect the sulphur in the steel.

This report was presented at The National Open Hearth Conference, AIME, Palmer House, Chicago, April 19.

Data were taken from 24 casts from blast furnaces which were arbitrarily operated to produce high-sulphur iron. The data included analysis of pig iron from top and bottom of transfer ladles, kish, slag and steel samples taken at all stages of production in the open hearth, and molten metal temperatures taken during significant periods.

The following facts were found and conclusions drawn:

(1) As the sulphur content of the iron increased, the sulphur drop in the transfer ladles increased, apparently in a straight line relationship (See fig. 1). This is probably due to the relationship between temperature and sulphur of the iron as covered in (5) below (See figs. 8 and 9).

(2) It was noted that high-sulphur iron was not produced when the manganese content was over 2.80 pct (Note points x in fig. 1).

(3) No relationship was found between sulphur in the iron and the melt and ladle sulphurs in the steel, as shown on figs. 2 and 3. This conclusion was substantiated by an analysis of the data from all heats produced in the four open hearth shops for the period June 5 to Dec. 25, 1948 (See fig. 4).

(4) For any given sulphur analysis of iron, when the manganese content was 2.80 pct or over, the sulphur drop in the iron-transfer ladles was approximately 20 points greater than it was for manganese contents under 2.80 pct. Only two exceptions were found where there was a sulphur pickup on high-manganese casts; there is probably a relationship between the short transit times involved, the sulphur in the coke used on top of the ladles and the sulphur pickup.

(5) In order to determine the effect of transit time on sulphur removal, casts were pigged at intervals of from 1 to 5 hr between ladles. The sulphur content and the temperature of the metal at time of pigging were recorded and plotted (See fig. 5). It is noted that there

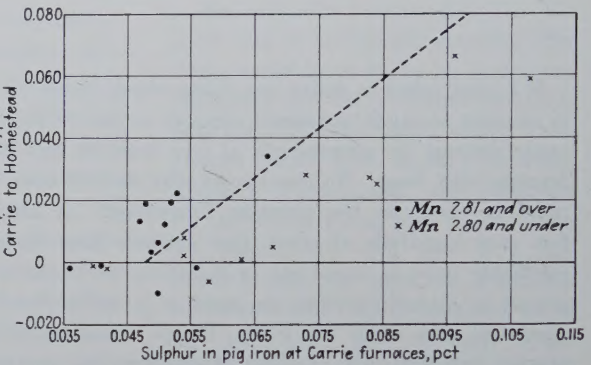


Fig. 1—Sulphur drop between Carrie and Homestead vs iron sulphur at Carrie. Data obtained from experimental casts sent to openhearth No. 4.

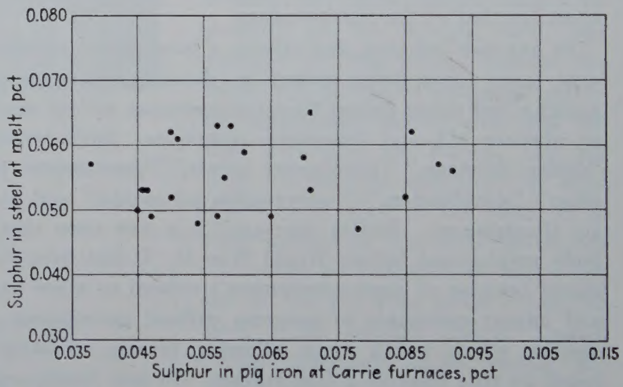


Fig. 2—Melt sulphur vs iron sulphur. Data obtained from experimental casts sent to openhearth No. 4.

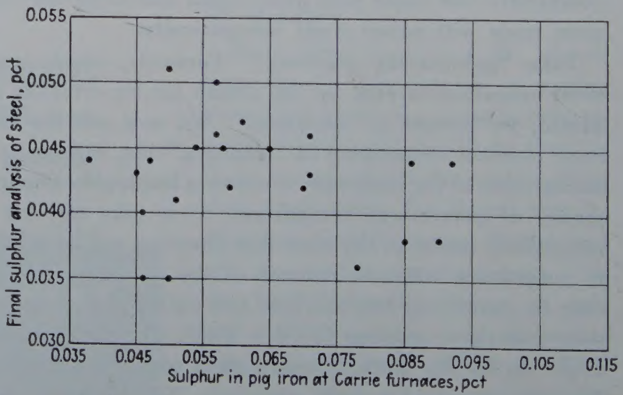


Fig. 3—Final sulphur analysis of steel vs iron sulphur at Carrie. Data obtained from experimental casts sent to openhearth No. 4.

is a direct relationship between percent sulphur in the iron at the pig machine and the temperature of iron at time of pigging. It is probable that the wide band of points, as shown on the chart, is due to errors in the taking of temperature with an optical pyrometer under varying light conditions, i.e., day and night. The low-sulphur points at high temperatures are undoubtedly the result of insufficient sulphur in the system to produce a high-sulphur analysis at any temperature. The sparsity of high-sulphur points on the curve at high temperatures is probably because high temperature furnace conditions are not conducive to the production of high-sulphur iron. A typical cast showed the following results:

	Pct S at Cast	Pct Mn at Cast	Time Cast to Time Pigged, Hr:Min.	Pct at Time Pigged, Position in Ladle		
				Top	Mid.	Bot.
Ladle No. 12	0.079	1.90	3:02	0.043	0.038	0.027
Ladle No. 22	0.065	1.82	1:59	0.069	....	0.046
Ladle No. 143	0.061	1.83	2:14	0.062	0.053	0.044
Ladle Nos. 7 & 133*	0.056	1.87	3:06	0.020	....	0.021

* No. 7 ladle was redumped into No. 133 ladle 2 hr 1 min after casting; No. 133 ladle was poured over pig machine 1 hr 5 min after being reladled.

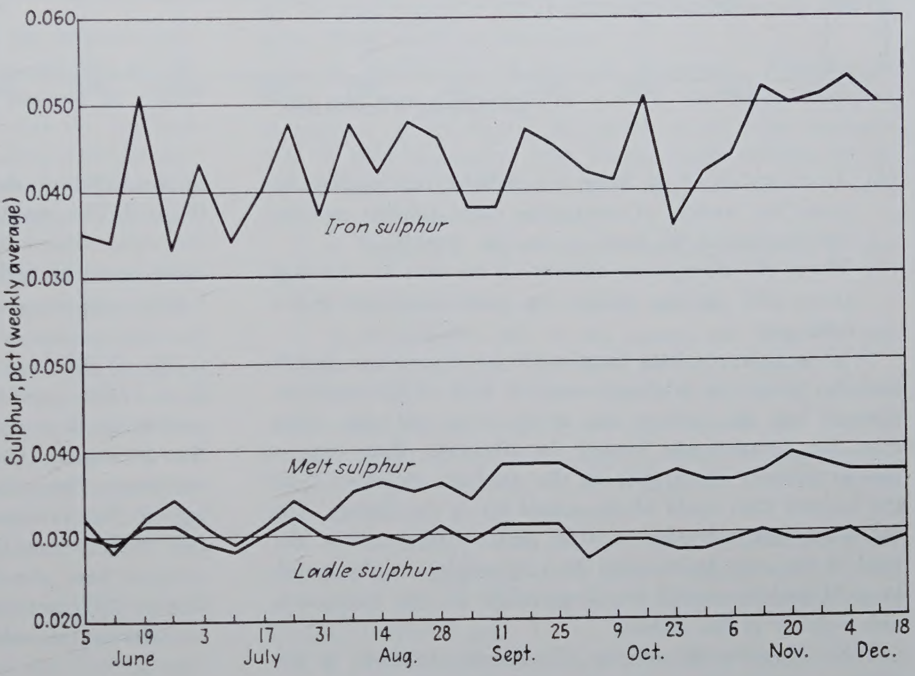


Fig. 4—Weekly average of iron sulphur, melt sulphur and ladle sulphur at Homestead No. 2 openhearth.

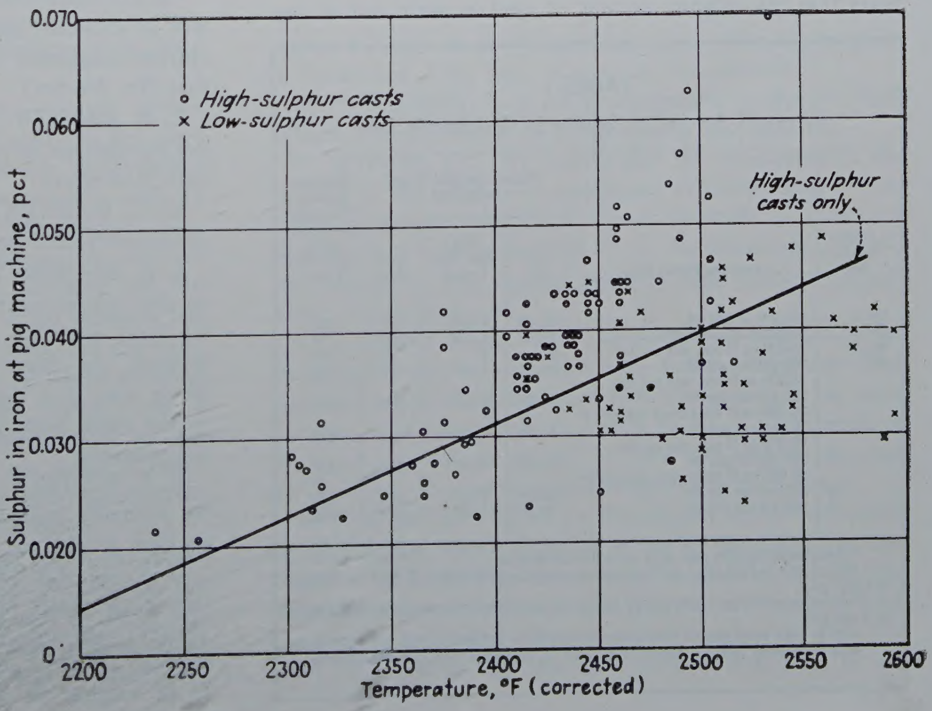


Fig. 5—Relationship between sulphur content and temperature of metal at time of pigging.

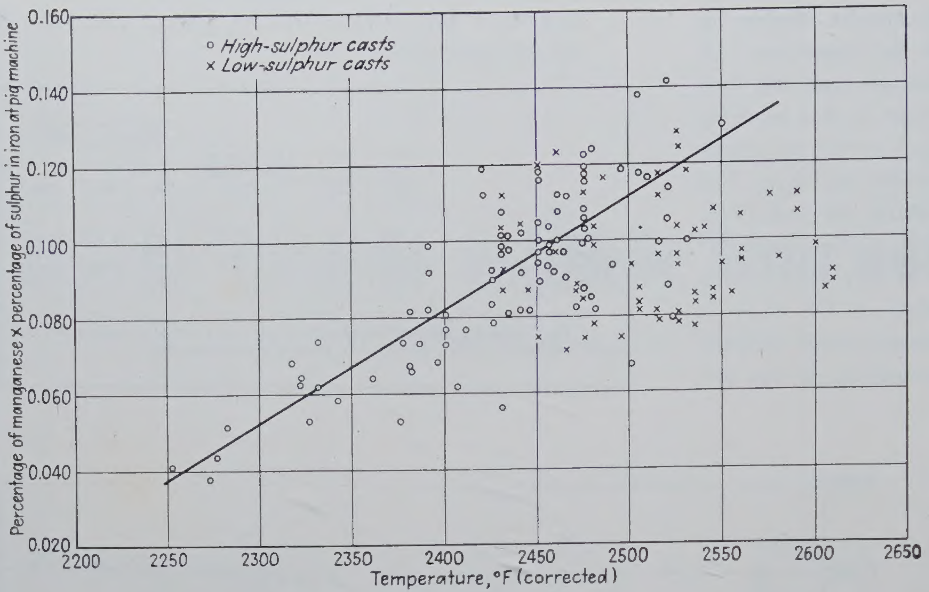


Fig. 6—Relationship between the product of manganese times sulphur and the temperature of the metal at the pig machine.

(6) As shown on fig. 6, there is a definite relationship between the product of manganese times sulphur and the temperature of the metal at the pig machine.

(7) Where the manganese content of the iron as cast was above 2.80 pct the sulphur in every case was below 0.065 pct.

Sulphur balances have been made on three open hearth furnaces where the sulphur content of each of the materials charged into the furnace and of the steel and slag taken from the furnace was known. In all cases, there was a greater amount of sulphur in the products removed from the furnace than could be accounted for in the charge. The difference was equivalent to 0.01 pct to 0.02 pct S in the steel. It can only be assumed that the sulphur in the metallurgical fuel consumed was responsible for the unaccountable sulphur in the system.

Table I shows the amount of sulphur contained in the different combinations of fuels as fired in the Homestead open hearth furnaces. It has been noted over a period of years that the sulphur content of steel at melt and at tap in the different shops varies as the sulphur contained in the fuel. This would indicate that it is not improbable that the unaccounted for sulphur difference mentioned above came from the fuel.

For comparison purposes, it might be pointed out that the total amount of the sulphur contained in all charge materials of the three sulphur balance heats ranged from 130 lb to 174 lb per heat. It requires 106 lb of sulphur in the steel to produce an 0.040 pct S analysis in the open hearth No. 4 furnaces (240,000 lb of product) where the study was made. Note that the sulphur introduced into the open hearth No. 4 furnaces with the different combinations of fuel ranges from 136 lb to 505 lb per heat. If all of this sulphur were absorbed by the steel, it would be equivalent to 0.057 pct. to 0.210 pct sulphur in the steel without considering the sulphur in the original charge.

TABLE I

Survey of Amount of Sulphur in Openhearth Fuels

Openhearth Shop	Average Firing Rate	Pounds Sulphur Fired with Fuel			Pounds Sulphur Charged per Heat, Using 0.080 Pct S Iron
		Per Hr	Per Net Ton Ingots	Per Heat	
No. 5	450 gal oil per hr	28.43	1.472	331	260
No. 3	50,000 cu ft coke gas per hr	40.44	7.264	540	72
No. 2	25,000 cu ft nat. gas per hr	0	0	0	60
No. 4—1	190 gal tar per hr 16,000 cu ft nat. gas per hr	15.01	1.447	171	132
2	200 gal tar per hr 30,000 cu ft coke oven gas per hr	40.08	4.277	505	132
3	190 gal oil per hr 16,000 cu ft nat. gas per hr	12.00	1.156*	136	132
4	200 gal oil per hr 30,000 cu ft coke oven gas per hr	36.90	3.981*	470	132
5	320 gal tar per hr	25.31	2.37	280	132
6	320 gal oil per hr	20.21	1.89	222	132

* Assume production rate with oil is the same as tar.

Pct sulphur in Fuel Oil: 0.79 pct by wt; sp gr = 0.959 A.P.I. @ 60°F = 0.06318 lb S per gal.

Pct sulphur in Tar: 0.78 pct by wt; sp gr = 1.216 A.P.I. @ 60°F = 0.079104 lb S per gal.

H_2S in coke oven gas = 5.67 grains per cu ft = 0.80877 lb H_2S per 1000 cu ft.

H_2S in natural gas: Amount of sulphur is negligible and can be overlooked.

DISCUSSION

CHAIRMAN LOUGHREY: Thank you, Mr. Warren, that was an excellent paper, and I am sure it should elicit some spirited comments. Is there anyone who would care to question Mr. Warren?

L. R. BERNER: I was intrigued by your figure of 2.81 pct manganese in your hot metal. Is that a regular analysis with Homestead?

H. E. WARREN: Our normal manganese content is approximately 2.65 pct.

L. R. BERNER: That is out of our world! Our people tell us that the manganese is going to shrink to 1 pct and if we want more we can get it by putting openhearth slag through the blast furnace and take higher phosphorus along with it. I don't know whether there are many here in the same boat, but that is our dish, and we don't like the prospect.

H. E. WARREN: With the manganese content mentioned, we normally operate around 0.375 pct phosphorus. We go as high as 0.4 pct.

H. L. ALLEN (Republic Steel Corp., Buffalo): The figures came pretty fast, but I managed to copy a couple and perhaps you can explain them. On the No. 2 shop, the average sulphurs were around 30 and you are putting 505 lb of sulphur in per heat. In the No. 3 openhearth, you are running in the 40's with 136 lb of sulphur. What is the significance?

H. E. WARREN: In the No. 2 shop, no sulphur goes in with the fuel. Natural gas is used. Table I shows an average firing weight of 25,000 cu ft of natural gas per hr. The figures on the right-hand side of Table I are the number of pounds of sulphur that would be put into the furnace with iron of 0.080 pct sulphur analysis. This shows what 0.080 pct sulphur in the iron, which we think is a high-sulphur iron, looks like compared to the sulphur we throw into the furnace with the fuel.

In the No. 3 shop, which uses coke oven gas, we burn 30,000 cu ft of gas per hr and 540 lb of sulphur per heat is thrown into the furnace. If we charged 60 pct pig (percentage based on iron and iron and steel scrap) only 72 lb of sulphur is charged in the furnace with iron of 0.08 pct sulphur analysis.

In the No. 4 shop, the figures vary with the different combinations of fuel, the highest one being at the rate of 200 gal of tar and 30,000 cu ft of coke oven gas per hr. Some 500 lb of sulphur is thrown into the heat with the fuel and only 132 lb of sulphur is charged when using 0.08 pct sulphur iron. This is five times as much sulphur with the fuel as we put in with what we consider high-sulphur iron. Does that answer you?

H. L. ALLEN: Would you then say that the fuel is the governing factor on the sulphur, or rather on ladle sulphur in your shops?

H. E. WARREN: Yes, definitely. We know that is a fact in our shops. The fuels shown here are the fuels we use all the time. No. 2 shop averages 0.026 pct to 0.030 pct sulphur in the final steel day in and day out, month in and month out, year in and year out. No. 4 shop averages 0.038 pct. No. 5 shop averages 0.030 pct and it varies exactly like that, regardless of the type of iron we charge in the furnace including 0.135 pct sulphur iron.

G. H. TODD (Armco Steel Corp., Ashland, Ky.): Our situation is pretty much like Louis Berner's except our manganese is 1.60 to 1.75 pct. We are not having any great degree of trouble with sulphur. I would like to ask you, Mr. Warren, to mention other advantages that there are with regard to your range of manganese, other than the benefits on sulphur, or, any disadvantages that there may be.

H. E. WARREN: Contrary to the belief of many people due to discussions over the last couple of years on the same subject, we as openhearth operators do not like high-sulphur iron. We needed iron badly in the openhearths, and, in order to get it, we had to put up with higher-sulphur iron. The blast furnaces increased their production by decreasing the slag volume in the furnace. We wondered why we could take 0.135 pct sulphur iron, let it go through the openhearths and come out with 0.025 pct, 0.030 pct and comparable sulphurs, depending on the shop in which we used it. We started out to find the reason. We normally use a lot of openhearth slag in our blast furnaces and we get approximtaely 2.65 pct manganese in our blast furnace iron all the time. There is an economy in using openhearth slag to recover the metallics in the blast furnace.

There have been many questions raised as to the cause of low mixer life. It is thought by many people that the increased manganese content of the iron and probably the slag from this iron are responsible for a reduction in mixer life. Naturally, with higher sulphur and higher manganese iron, the yield goes down. We do it strictly as an economy measure at Homestead. We think we gain something from the practice, particularly an increase in iron production during bad scrap periods.

G. H. TODD: Let me be more specific. I begin to understand your conditions at Homestead a little better now. Is there any difference noticed in the flushing qualities of your slag from the higher manganese as compared to the flush when using lower manganese pig iron?

H. E. WARREN: I would say no.

G. H. TODD: Did you experience any great change in melting practice with the higher manganese?

H. E. WARREN: No. With all this as you probably know, we have a long distance to travel between our blast furnaces and our openhearth shops. This report shows that the longer you hold it in the ladles, the lower the sulphur is by the time it gets to the openhearth. Of course, we pick up some skull, which we don't like.

G. B. McMEANS (Kaiser Co., Fontana): Contrary to what has been discussed, we see no advantage in higher manganese in hot metal. Hot metal at our plant averages 0.45 to 0.50 manganese with average melt sulphur of approximately 0.055. Finished ladle sulphurs have averaged 0.029 for the last two months.

H. E. WARREN: How many pounds of limestone do you use?

G. B. McMEANS: Close to 200 lb per ton.

H. E. WARREN: All of our figures are from the use of 80 lb to 120 lb of raw limestone per ton of ingots.

L. I. FIELD (U. S. Patent Office): I wanted to ask you when you held the iron for the pig machine and got the sulphur drop, did you get a loss of silicon or manganese? When you held the iron, did the manganese drop off in the same proportion as the sulphur?

H. E. WARREN: With the first ladle I mentioned as an example, the manganese at the time of casting was 1.90 pct, at pigging time it was 1.83 pct, 1.86 pct, 1.85 pct, or it dropped 0.04 of 1 pct.

L. I. FIELD: Did you have a mechanism figured out for sulphur removal? How do you think it comes off?

H. E. WARREN: As far as we know it follows temperature.

L. I. FIELD: As the temperature goes down, the sulphur is thrown out of the iron. Is it as an iron sulphide?

H. E. WARREN: I am not a metallurgist or chemist. Phil Schane is here. Maybe he could answer that question.

P. SCHANE, JR.: We believe that the mechanism is the removal of the sulphur as manganese sulphide. Most of you know manganese sulphide is almost insoluble in steel and iron and is a solid up to 2900 F. As the temperature drops, the manganese and sulphur react to form manganese sulphide, which floats out.

L. I. FIELD: Thank you. You showed no correlation between your cast sulphur and your finished sulphur. Was that because you added to your lime charge where you were carrying a heavy sulphur fuel such as No. 5 openhearth or do you figure 820 lb per ton of lime was uniform through all the shops, that is, they were scattered in their range.

H. E. WARREN: We throw the sulphur out of the system by flushing off, which we think is one of the major requirements in openhearth practice to get sulphur out of the system. Because we do have what we consider a good flush practice to get rid of silica, phosphorus, etc., the iron sulphur having risen into the blast furnace iron slag, by the time it goes into the openhearth furnace, it goes into the slag and out the flush hole. When our lime comes up, it does not have to take care of those acids, therefore, we have a low lime consumption.

L. I. FIELD: Thank you.

L. P. LIAS (Jones & Laughlin Steel Corp., Cleveland): We certainly have had a very vigorous discussion on this subject and I am sure it is conducive to a lot of thought. There have been a lot of conclusions drawn and disagreed with. I think that there is one very significant factor in this whole picture that has been neglected which will throw these conclusions way out of line and that is the amount of sulphur in the scrap charge. I think that is a very significant factor and I think it is going to distort these figures.

H. L. TEAR (Jones & Laughlin Steel Corp., Pittsburgh): This has been a most lively discussion so far. There were two questions asked and I may be able to provide the answers, as based on our experiences. First was the question covering the effect of bath sulphur content on production rate. We follow this each month and the results for the first three months' total heats show the following results, using a 0.040 pct sulphur preliminary as the base:

Preliminary Sul. Range	*Pct Loss in Production Rate*
0.040 & under	—
0.041 to 0.050	2.70
0.051 to 0.060	5.50
0.061 to 0.070	7.70
0.071 & over	9.20

We also have a good deal of experience with various types of scrap and the answer to the question of "What effect does the scrap have on sulphur preliminaries?" can only be given as "plenty." We charge scrap varying from 0.020 pct to 0.350 pct sulphur, the high sulphur material coming from our bessemer screw and openhearth free-machining steels and our tonnages in these grades is considerable. Our preliminary sulphurs for the first three months of this year ranged from 0.024 pct to 0.167 pct and in this shop we make 60 pct of our heats to a 0.025 pct sulphur limit.

The question on amount of limestone used and the amount of sulphur which can be removed is one that always gives rise to considerable debate. During the year 1948 we used an average of 106 lb of limestone per ton of charge and worked the heats with burnt lime. The amount of sulphur removed is shown in the following table.

Preliminary Sul. Range	*Ave. Sul. Content*	*Ave. Ladle Anal.*	*Pct of Sul. Removed*
0.040 & under	0.0362	0.0251	30.6
0.041 to 0.050	0.0475	0.0266	41.5
0.051 to 0.060	0.0558	0.0288	48.3
0.061 to 0.070	0.0654	0.0307	53.0
0.071 & over	0.0814	0.0343	57.8

To remove sulphur in the openhearth furnace is a costly undertaking. However, it can be done if you are willing to take the penalty in production rate, flux costs and bottom maintenance time. Sulphur removal needs reducing conditions and here we are with an oxidizing process which makes the problem that much tougher. We aim to overcome this by using large slag volumes and to get this we feed plenty of burnt lime and sand. The following table illustrates the increase needed in burnt lime additions as the sulphur specifications are lowered. The period covered is the first three months of this year and using 0.040 sulphur specification as the base:

Spec. Lad. Sul. Limits	*Pct of Total Hts. Made*	*Pct Increase in Burnt Lime Add.*	*Ave. "V" Values*
0.040	3.6	——	2.5
0.035	10.2	5.00	2.6
0.030	23.8	30.80	2.8
0.025	62.4	62.50	2.9

As to the effect of flush off, we do not have any in this shop, but we do on our large tilting furnaces. The lime consumption on our tilting furnaces is very much lower than on the stationaries. This permits flushing of the undesirable high silica slags and allows us to keep much "sweeter" slags over the bath. In fact, the whole problem of sulphur removal is closely related to the concentration of sulphur in the slag and we feel that this is one of the most important items to watch. Generally speaking, the subject can be summed up in saying that one can get the sulphur content down to where he needs it, if he is willing to pay the price in production rate and flux costs, etc.

H. E. WARREN: From the comments that have been made, there might be a lot of doubt in people's minds. This paper only covered the sulphur in metal and touched on the effect of sulphur in the fuel. The sulphur from other sources such as scrap is an altogether different problem. We do not get the sulphur drops from the use of high sulphur scrap that we get with the same amount of sulphur in the iron. It is a different problem altogether.

V. W. JONES (Armco Steel Corp., Middletown): I want to clear up something, in this matter of the effect of hot metal sulphur on ladle sulphur, when you are referring to a 100 sulphur in your metal, that doesn't necessarily mean that the sulphur you have in the metal is being charged into the open hearth, isn't that right?

H. E. WARREN: Our normal procedure for reporting sulphur is as taken from the runner at the blast furnaces. When I said 0.1 pct sulphur or 0.135 pct sulphur, that is as it comes out of the blast furnace. We do not normally analyze the iron as it goes into the openhearth furnace and for the figures I gave here today, we took the analyses at the runner and then we took them again at the openhearth furnace from the bottom, middle and top of the transfer ladles, and in some cases we took it as it went into the openhearth furnace. We found that the longer time between the time at cast and time of charge in the furnace, the less sulphur we had in the iron.

M. TENENBAUM (Inland Steel Co., East Chicago, Indiana): Two years ago Mr. Warren presented some rather surprising results obtained at his plant that indicated very little relationship between hot metal sulphur (samples at the blast furnace) and the residual sulphur content in the openhearth furnace. These results appeared to be very much contrary to general experience in the industry. It appears from the data given today that the quoted hot metal sulphur analysis was not the true analysis of the metal charged into the furnace; much of the original hot metal sulphur being eliminated during transfer from blast furnaces to open hearth. Mr. Warren should be complimented for his conscientious and successful effort to explain the apparent difference between his earlier results and other reported data.

Addenda

Metals Branch Committee

When listing officers and committees of Metals Branch Divisions, AIME, on Pages 14 and 15, Sect. 1, JOURNAL OF METALS for June, the following names were omitted, hence are published herewith:

EXTRACTIVE METALLURGY DIVISION

FINANCE

Hugh M. Shepard, *Chairman*

C. C. Long
J. D. Sullivan

MEMBERSHIP

Robert H. Ridgway, *Chairman*

Michael B. Bever
P. C. Feddersen
W. H. Goodrich
L. L. McDaniel
R. R. McNaughton
A. W. Schlechten
E. McL. Tittman
R. H. Waddington
S. R. Zimmerley
Richard A. Young

PYROMETALLURGY

P. D. Honeyman, *Chairman*

R. D. Bradford
E. M. Bunce
R. B. Caples
R. G. Knickerbocker
E. L. McDaniel
B. M. O'Harra
O. C. Ralston
B. L. Sackett
C. N. Schuette
E. M. Tittman

IRON AND STEEL DIVISION

FERROALLOY

R. F. Mather, *Chairman*

A. Linz and S. M. Norwood
(additions)

BLAST FURNACE, COKE OVEN AND RAW MATERIALS FINANCE SUBCOMMITTEE

E. F. Mitchell, *Chairman*

P. L. Edwards
M. E. Nickel
V. J. Nolan
J. F. O'Brien
H. A. White
C. L. Wyman

Power Metallurgy Men Hold "Town Meeting"

A panel of six experts on powder metallurgy took part at the June meeting, the third gathering of the year of the New York district, AIME. A thoroughly practical discussion was held and a new approach was tried by organizing a powder metallurgy "Town Meeting." The practical phases of the subject were in contrast to more theoretical and scientific phases of the first two meetings of the season. Fred P. Peters, vice president, Reinhold Publishing Corp., served as moderator.

William Toeplitz, vice president, Bound Brook Oil-less Bearing Co., emphasized the fact that many parts made by powder metallurgy do not meet the tolerances specified by the user. He suggested that closer cooperation between vendor and purchaser and possible standardization would remedy this difficulty.

George Stern, director of research, American Electro Metal Corp., emphasized the need for careful quality control in the production of stressed parts by powder metallurgy. Whereas in manufacture of comparatively simple products such as oil-less bearings, the matter of metallurgical control is based on years of experience, new methods and constant vigilance are required in the manufacture of structural parts. This is particularly true of complicated mechanical design or metallurgical specifications.

Based on his experience in mass production of sintered parts, J. L. Bonano, chief engineer, Lionel Corp., analyzed the cost picture. He demonstrated that by integration of powder metallurgy equipment into an existing production line substantial savings can be realized. This is particularly true when quantities are so high that the manufacturer can absorb the cost of experimental dies and production dies, the latter usually being made with carbide inserts.

More information on tooling was given by Irving Donahue, plant superintendent, Presmet Corp. He also called for more lively exchange of information among the practical men in powder metallurgy.

The all-important problem of testing the properties of powder metallurgy materials and parts was discussed by Dr. C. G. Goetzel, vice president and director of research, Sintercast Corp. of America. He brought out the point that sampling is a most important phase of this work because most tests are destructive and cannot therefore be performed on all or even many finished parts. Some of the principles which must underlie test procedures were outlined and the need for standardization was made clear.

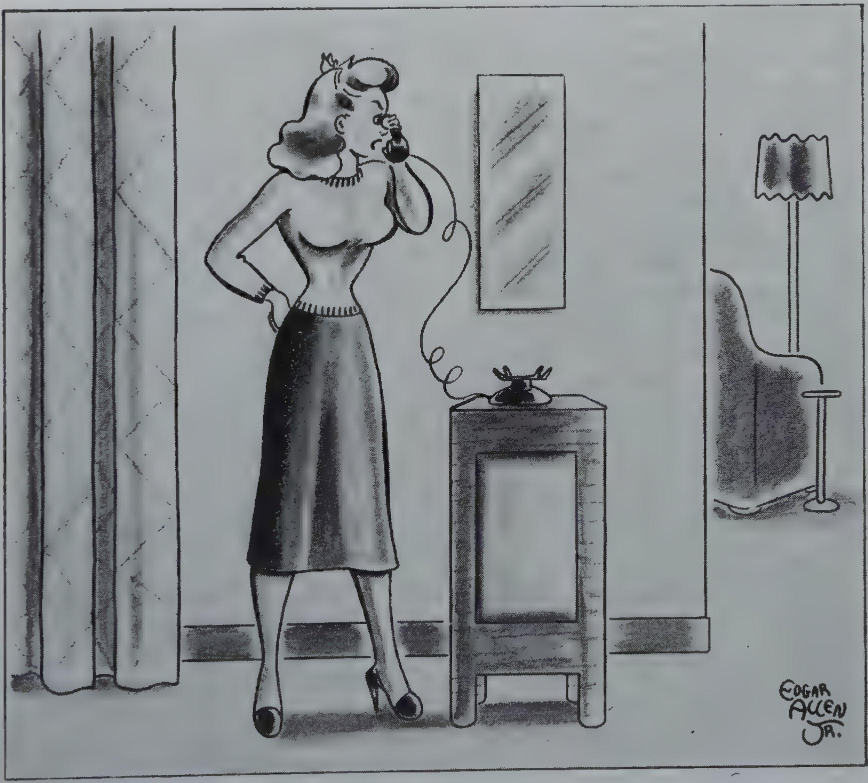
The discussion, which was ably directed by Mr. Peters, brought out many more interesting points not covered by the speakers. The meeting had to be closed with many questions deferred for another get-together.

The next meeting is tentatively scheduled for September 14.

RICHARD P. SEELIG

SMELTS and SMILES

By Edgar Allen, Jr.


EDGAR ALLEN JR.

"You have to work again? Well, okay, if you think more of your old solution of tetrasodium pyrophosphate, zinc sulphate, potassium fluoride, and potassium carbonate than you do of me!"

Tentative Papers, Fall Meeting, IMD

The following is a tentative list of papers to be presented at the Fall meeting of the Institute of Metals Div. at the Hotel Allerton, Cleveland, in connection with the National Metal Congress, Oct. 17, 18 and 19.

INSTITUTE OF METALS DIVISION

Stable Transformation Nuclei in Solids, *J. N. Hobstetter.*

The Pore Size of Hydrogen Reduced Tungsten Powder, *Bernard Kopelman* and *C. C. Gregg.*

Electrical Properties of the Intermetallic Compounds Mg_2Sn and Mg_2Pb, *W. D. Robertson* and *H. H. Uhlig.*

Stress and Strain States in Elliptical Bulges, *C. C. Chow, A. W. Dana,* and *G. Sachs.*

A Method of Examination of Sections of Fine Metal Powder Particles with the Electron Microscope, *Miss Laurence Delisle.*

Precipitation Phenomena in the Solid Solutions of Nitrogen and Carbon in Alpha Iron Below the Eutectoid Temperature, *L. J. Dijkstra.*

Recrystallization and Microstructure of Aluminum - Killed Deep Drawing Steel, *R. L. Rickett, S. H. Kalin,* and *J. T. MacKenzie, Jr.*

The Effect of Ferrite Grain Size on Notch Toughness, *J. M. Hodge, R. D. Manning,* and *H. M. Reichhold.*

The Hardenability Effect of Molybdenum, *J. M. Hodge, J. L. Giove,* and *R. G. Storm.*

The Beryllium-Iron System, *R. J. Teitel* and *M. Cohen.*

The Crystal Structure of Ni_4W, *E. Epremian* and *D. Harker.*

Microstructures of Silicon Ingots, *W. G. Pfann* and *J. H. Scaff.*

P-type and N-type Silicon and the Formation of the Photovoltaic Barrier in Silicon Ingots, *J. H. Scaff, H. C. Theurer,* and *E. E. Schumacher.*

Investigation of Temper Brittleness in Low-Alloy Steels, *S. A. Herres, A. R. Elsea.*

Oriented Arrangements of Thin Aluminum Films on Ionic Substrates, *Thor Rhodin, Jr.*

The Comparative Creep Properties of Several Types of Commercial Coppers, *A. D. Schwope, K. F. Smith,* and *L. R. Jackson.*

The Vapor Pressures of Zinc and Cadmium Over Some of Their Silver Alloys, *C. E. Birchenall* and *C. H. Cheng.*

Transformation of Gamma to Alpha Manganese, *E. V. Potter, H. C. Lukens,* and *R. W. Huber.*

The Rapid Determination of Orientations of Cubic Crystals, *C. G. Dunn* and *W. W. Martin.*

The Study of Grain Boundaries with the Electron Microscope, *J. F. Radavich.*

Liquid Solubility of Manganese in a Magnesium-Aluminum-Tin Alloy, *B. J. Nelson* and *G. F. Sager.*

Secondary Recrystallization in Copper, *M. L. Kronberg* and *F. H. Wilson.*

Electrical Resistivity Measurements on Iron-Silicon Compacts Prepared by the Powder Metallurgy Procedure, *F. W. Glaser.*

Ferromagnetic Alloys in the Systems Copper-Manganese-Indium and Copper-Manganese-Gallium, *F. A. Hames,* and *D. S. Eppelsheimer.*

A Metallographic Description of Fracture in Impact Specimens of a Structural Steel. *M. Baeyertz, W. F. Craig, Jr.,* and *E. S. Bumps.*

Recovery and Recrystallization in Brass, *B. L. Averbach.*

Kinetics of the Reactions of Zirconium with O_2, N_2 and H_2, *E. A. Gulbransen* and *K. Andrew.*

The Effect of Quenching on the Age Hardening of Two Aluminum Alloys, *R. D. Barer* and *M. B. Bever.*

The Effects of Molybdenum and Commercial Ranges of Phosphorus on the Toughness of 0.40 Pct. Carbon Chromium Steels, *M. Baeyertz, W. F. Craig, Jr.,* and *J. P. Sheehan.*

The Active Slip Systems in the Simple Axial Extension of Single Crystalline Alpha Brass, *Robert Maddin, C. H. Mathewson,* and *W. R. Hibbard, Jr.*

Annealing Twins in Copper and 70-30 Alpha Brass, *W. R. Hibbard, Jr., You-Chao Liu,* and *Stanley F. Reiter.*

The Lattice Parameters of High Purity Alpha Titanium; and the Effects of Oxygen and Nitrogen on Them, *H. T. Clark, Jr.*

Magnesium-Titanium Systems, *K. T. Aust* and *L. M. Pidgeon.*

Discontinuous Crack Propagation—Further Studies, *L. D. Jaffe, E. L. Reed,* and *H. C. Mann.*

The Effect of Oxygen, Nitrogen, and Hydrogen on Iodide Refined Titanium, *R. I. Jaffee* and *I. E. Campbell.*

Recrystallization Texture and Coarsening Texture in High Purity Aluminum, *P. A. Beck* and *Hsun Ju.*

Analysis of Interstitial Diffusion Using Activity Methods, *A. G. Guy.*

The Origin of Annealing Twins in Brass, *Robert Maddin, C. H. Mathewson* and *W. R. Hibbard, Jr.*

The Yielding and Strain-Aging of Carburized and Nitrided Single Crystals of Iron, *H. Schwartzbart* and *J. R. Low, Jr.*

A Dilatometric Study of the Sintering of Metal Powder Compacts, *Pol Duwez,* and *Howard Martens.*

The Transformation in B—CuAl Alloys, *E. P. Klier* and *S. M. Grymko.*

Kinetics of Austenite Decomposition: Ferrite Nucleated Products, *J. C. Fisher, J. H. Hollomon,* and *D. Turnbull.*

Size Effects in Quenching High-Purity, Precipitation - Hardenable Alloys, *W. L. Finlay.*

The Transverse Bending of Single Crystals of Aluminum, *M. K. Yen* and *W. R. Hibbard, Jr.*

The Diffusion and Solubility of Carbon in Alpha Iron, *J. K. Stanley.*

The Isolation of Carbides from High Speed Steel, *D. J. Blickwede* and *M. Cohen.*

Surface Orientation and Rolling of Magnesium Sheet, *R. L. Dietrich.*

Metallographic Examination of Beryllium Alloys, *M. C. Udy, G. K. Manning,* and *L. W. Eastwood.*

The Ternary System, Copper-Manganese-Zinc, *T. R. Graham, J. R. Long,* and *C. E. Armantrout.*

Studies of Interface Energies in Some Aluminum and Copper Alloys, *K. K. Ikeuye* and *C. S. Smith.*

Stages in the Deformation of Monel Metal as Shown by Polarized Light, *D. H. Woodard.*

Influence of Temperature on the Stress-Strain-Energy Relationship for Copper and Nickel-Copper Alloys, *D. J. McAdam.*

Free Energy Change Accompanying the Martensite Transformation in Steels, *John C. Fisher.*

Determination of Boundary Stresses During the Compression of Cylindrical Powder Compacts, *M. E. Shank* and *John Wulff.*

Structure of Diborides of Titanium, Zirconium, Columbium, Tantalum and Vanadium, *J. T. Norton, H. Blumenthal,* and *S. J. Sindeband.*

Structure and Nature of Kink Bands in Zinc, *J. B. Hess* and *C. S. Barrett.*

Simultaneous Aging and Deformation in Metals, *J. D. Lubahn.*

Preparation and Casting of Beryllium Melts, *J. G. Kura, J. H. Jackson, M. C. Udy,* and *L. W. Eastwood.*

ALL INSTITUTE SECTION

APPEARING IN:
• MINING ENGINEERING
• JOURNAL OF METALS
• JOURNAL OF PETROLEUM TECHNOLOGY

More Students in Mineral Engineering Courses

By **WILLIAM B. PLANK AND EDWARD MARTINEZ** • HEAD DEPARTMENT OF MINING AND METALLURGICAL ENGINEERING AND ASSISTANT PROFESSOR IN MINING, RESPECTIVELY, LAFAYETTE COLLEGE.

There were 15,028 students enrolled in mineral engineering courses on Dec. 1, 1948, in the United States and Canadian colleges, as revealed by the ninth biennial questionnaire study made by the writers under the auspices of the Mineral Industry Education Division of the AIME. Sixty-four colleges in the United States and eight in Canada are covered by the study.

Every mineral engineering school in both countries is represented in the study and for that reason the data are comparable with former studies. As formerly, the general enrollment figures are included, taken this year from the February, 1949, issue of the *Journal of Engineering Education.*

The combined enrollment of 15,028 mineral engineers in both countries is 16.6 percent larger than the enrollment of 12,892 in 1946-1947. There was an increase of 20 percent in the United States figures, but a decrease of 14 percent in the Canadian figures during this period. These comparisons are shown in Tables 1 and 2.

The current total enrollment of 249,913 engineers of all kinds in the United States and Canadian colleges, shown in the data supplied by the ASEE in Table 3, is 12 percent greater than the 222,557 enrollment in 1946-47. The mineral engineering group of both countries showed a growth of 16.6 percent during the same period. As compared with 1947-48, however, the total engineering enrollment decreased about 1 percent, whereas the mineral engineering enrollment increased 22 percent to an all-time peak, thus maintaining a steady growth that was begun right after the war.

The number of first degrees in engineering conferred in 1946-47, as shown in Table 4, was 19,272 and in 1947-48, 30,018. It has been estimated that this year at least 40,000 engineers will be graduated and probably the same number will graduate next year. This year 2881 mineral engineers in both countries will receive their first degrees and the number will probably be larger next year. Thus it is seen that the deficit in the supply of engineers caused by the war is being met rapidly.

An indication of the possible trend in engineering enrollment can be seen in the decrease in the size of the freshman classes over these two years as shown in Table 3. In 1946-47, the total number of freshman engineers of all kinds in the United States and Canada was 84,652, whereas this year the group numbers 49,017. This is a decrease of 42 percent. The decrease in the number of mineral engineering freshmen during the same period, however, was from 4933 to 3090, or 37 percent.

Eventually, the decline in veteran enrollment and the lower birth rate during the war, of which these figures are an indication, will materially reduce the size of the engineering student groups of all kinds. S. C. Hollister, of Cornell University, estimates that the number of entering freshman engineers is undergoing a normal readjustment which by 1952-53 will

TABLE 1. MINERAL ENGINEERING STUDENT ENROLLMENT BY COURSES—1948-49, UNITED STATES, 64 SCHOOLS

Course	Freshman	Sophomore	Junior	Senior	Total Under-graduates	Graduate Students	Grand Total	Candidate B.S. Degree
Mining	481	544	517	456	1,998	82	2,080	426
Metallurgy	649	836	1,008	815	3,308	552	3,860	789
Petrol. and Nat. Gas	1,024	1,076	1,151	752	4,003	91	4,094	709
Ceramic	181	264	315	251	1,011	164	1,175	227
Geology	553	611	698	401	2,263	197	2,460	379
Fuels	6	8	9	8	31	16	47	8
Specials	......	......	......	......	53	......	53	......
Totals	2,894	3,339	3,698	2,683	12,667	1,102	13,769	2,538

Revision of a paper read before Mineral Industry Education Division, AIME, San Francisco, Calif., Feb. 14, 1949.

Table 2. Mineral Engineering Student Enrollment by Courses—1948-49, Canada, 8 Schools

Course	Freshman	Sophomore	Junior	Senior	Total Undergraduates	Graduate Students	Grand Total	Candidate B.S. Degree
Mining	99	112	163	178	552	0	552	172
Metallurgy	43	68	99	77	287	11	298	77
Petrol. and Nat. Gas	13	23	17	0	53	0	53	0
Ceramics	5	13	8	11	37	2	39	11
Geology	36	65	76	83	260	57	317	83
Totals	196	281	363	349	1,189	70	1,259	343

Table 3. Engineering Enrollment by Classes and Courses—1948-49, 151 United States and 6 Canadian Schools

Course	Freshman	Sophomore	Junior	Senior	5th Year and Others	Total Undergraduates	Graduate Students	Grand Total
Mining	427	576	637	527	6	2,173	83	2,256
Metallurgy	493	819	1,058	871	127	3,368	687	4,055
Petrol. and Nat. Gas	921	1,186	1,309	916	105	4,437	96	4,533
Ceramics	161	264	319	247	95	1,086	120	1,206
Total Mineral Engineers[1] U.S. and Canada	2,002	2,845	3,323	2,561	333	11,064	986	12,050
Chemical	3,722	5,095	5,955	4,784	1,692	21,248	2,371	23,619
Civil	5,522	8,139	9,483	7,113	1,541	31,798	2,063	33,861
Mechanical	7,725	12,446	15,390	12,093	3,453	51,107	2,535	53,642
Electrical	7,416	11,830	15,725	11,440	3,496	49,907	3,867	63,774
Other Engineers	19,080	12,855	11,921	9,280	8,912	62,048	3,801	65,849
In Extension Centers	3,550	1,869	730	514	455	7,118	......	7,118
Total Engineers U. S. and Canada	49,017	55,079	62,527	47,785	19,882	234,290[2]	15,623	249,913
Veterans, U. S. and Canada	15,282	28,011	42,959	33,969	12,183	132,394	5,880	138,274

[1] Geological and Fuel Engineers included in "Other Engineers".

[2] Includes 1210 women.

Table 5. Engineering Student Enrollment by Courses—Undergraduates and Graduates—1940-41 to 1948-49

	(1) 1940-41	(1) 1944-45	(1) 1946-47	(1) 1947-48	(2) 1948-49	(3) 1948-49
Mining	1,978	224	2,302	2,459	2,256	2,632
Metallurgy	2,450	472	3,179	4,121	4,055	4,158
Petrol. and Nat. Gas	2,877	376	3,048	4,665	4,533	4,147
Ceramics	843	190	940	1,108	1,206	1,214
Geology	792	?	?	?	?	2,777
Fuels	44	?	?	?	?	47
Specials	149	?	?	?	?	53
Total Mineral Engineers:						
United States	9,133	......	......	......	......	13,769
Canada	......	......	......	......	......	1,259
U. S. and Canada	......	1,262	9,469	12,353	12,050	15,028
Chemical	......	5,082	23,600	26,972	23,619	......
Civil	......	3,537	30,079	31,849	33,861	......
Mechanical	......	6,965	44,403	56,551	53,642	......
Electrical	......	5,934	38,963	56,408	53,774	......
Others	......	18,852	66,475	68,117	72,969	......
Total Engineers	114,116	41,632	222,557*	252,250	249,913	......

[1] Mining & Metallurgy, April 1948, U. S. and Canada.

2 Journal of Engineering Education, Feb. 1949, U. S. and Canada.

[3] Study of Mineral Education Division, AIME, Dec. 1, 1948.

* Includes 9568 Canadian undergraduate students, unclassified.

Table 4. First Degrees Conferred, All Engineers, United States and Canada

1942-43	14,714
1943-44	11,155
1944-45	4,724
1945-46	8,219
1946-47	19,272
1947-48	30,018

bring the number of graduations down to the prewar gradient of steady upward growth.[1]

The percentage of veterans studying engineering in both countries dropped from 57 percent of the total last year to 55 percent this year. This year 31 percent of the freshman engineers are veterans compared to 42 percent last year.

Among the mineral engineers in the United States, the petroleum and natural gas engineers maintain their position as the largest group, with 4094 students. They are followed closely, however, by the metallurgists with 3860 students. Next in rank are the geological engineers and mining geologists, listed under the title "Geology" in the tables, with 2460 students. The mining engineers rank fourth, numbering 2080 students, and the ceramic engineers are fifth in rank, with 1052 students.

Of significance to employers of mineral engineers in the United States is the fact that there are available for positions in the mineral industries only 2538 bachelors and about 500 graduates from this year's class. As usual, however, not all of these men will be available for jobs since a number will go into teaching, graduate schools, or other industries.

Employment opportunities for this year's mineral engineering graduates generally have been good but with a slower demand for men in the industries affected by the present slowing up of production. Demand for mining engineers in the east is reported to be better than elsewhere especially by the iron ore and the coal industries.

The employment situation for other engineers who graduated this year has not been so favorable. Deans of engineering schools say that all graduates will be placed but not as rapidly as in recent years. It has been estimated that out of the 40,000 engineers who graduated this year only 24,000 will be absorbed by industry, leaving a surplus of 16,000. It is believed that of the many factors that may cause a sharp upward trend in engineering employment of all kinds are the wider use of technology, the use of engineers in other professions, and above all, the increasing number of engineering problems involved in winning from the earth, the sea, and the air, the raw mineral materials upon which our highly industrialized civilization depends.

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[1] Postwar Engineering Enrollment, Journal of Engineering Education, March, 1949.

Table 6. Distribution of Graduate Students in Mineral Engineering—United States, 1933-34 to 1948-49

	1933-1934	1934-1935	1936-1937	1938-1939	1940-1941	1942-1943	1946-1947	1948-1949
Mining	40	55	49	44	44	20	70	82
Metallurgy	116	93	131	172	215	137	470	552
Petrol and Nat. Gas	18	29	58	43	75	27	187	91
Ceramics	19	36	48	64	50	19	138	164
Geology	46	62	34	86	127	9	127	197
Fuels	4	10	18	6	9	10	16	16
Totals	243	285	338	415	520	222	1,008	1,102

Data from Mineral Industry Education Division, AIME, studies.

Directory of Mineral Engineering Schools in the United States and Canada

**Accredited by ECPD, October, 1948*

The name and address of the school are given, followed by the length of the regular undergraduate curriculum, the degree granted, types of courses given, and the name of the man in charge. This covers only work for the first or Bachelor degree in each case. School catalogs should be consulted for details.

The following abbreviations are used:

A.	Arts
B.	Bachelor
Cer.	Ceramics or Ceramic
E.	Engineer or Engineering
Eng.	Engineering or Engineer
Eco.	Economic
Geol.	Geologist, Geological, or Geology
M.	Mines or Mining
Met.	Metallurgy or Metallurgical
Min.	Mineral
Mng.	Mining
M.S.	Master of Science
Pet.	Petroleum
Ref.	Refining
S.	Science
Tech.	Technology or Technical

UNITED STATES

University of Alabama, University, Ala. 4-yr. B.S. in: (1) *Mng. Eng., (2) Met. Eng., (3) Met., (4) Cer., (5) Pet. Tech. James R. Cudworth, dean; J. W. Stewart, head, School of Mines; T. N. McVay, head, Dept. of Ceramics.

University of Alaska, College, Alaska. 4-yr. or 5-yr. B.S. major in: (1) *Mng. Eng., (2) *Mng. Eng., Geol. option, (3) *Mng. Eng., Met. option. Richard C. Ragle, head, Dept. of Geology; Earl H. Beistline, head, Dept. of Min. & Met.

University of Arizona, Tucson, Ariz. 4-yr. B.S. in: (1) *Mng. Eng., (2) Met. Eng., (3) Mng. Geol. (4) Geol. T. G. Chapman, dean, College of Mines.

Polytechnic Institute of Brooklyn, Brooklyn 2, N. Y. 4-yr. B.Met.E. Otto H. Henry, professor of Metallurgical Engineering.

University of California, Berkeley, Calif. 4-yr. degrees in: (1) *Mng. Eng., (2) *Met., (3) *Pet. Eng., (4) Mineral Exploration. Lester C. Uren, chairman, Division of Mineral Technology.

Carnegie Institute of Technology, Pittsburgh, Pa. 4-yr. B.S. in *Met. Eng. Robert F. Mehl, head, Dept. of Metallurgical Engineering.

Case Institute of Technology, Cleveland, Ohio. 4-yr. B.S. in *Met. Eng. K. H. Donaldson, head, Dept. of Metallurgical Engineering.

University of Cincinnati, Cincinnati, Ohio. 5-yr. *Met. Eng. Cooperative. Dr. Roy O. McDuffie, professor of Metallurgy.

Colorado School of Mines, Golden, Colo. 4-yr. (1) *E.M., (2) *Geol. Eng., (3) *Pet. Eng., (4) *Met. Eng., (5) Pet. Ref. Eng. Ben H. Parker, president.

Columbia University, New York, N. Y. 4 or 5-yr. B.S. in (1) *Mng. Eng., (2) *Met. Eng., (3) Mineral Eng. Philip B. Bucky, prof. of Mining and Exec. Officer of Dept. of Mng., Met. and Min. Eng.

Cornell University, Ithaca, N. Y. 5-yr. B.Met.E. Fred H. Rhodes, director of the School of Chemical & Met. Eng.; S. C. Hollister, dean of the College of Engr.

Drexel Institute of Technology, Philadelphia 4, Pa. 5-yr. (co-operative) B.S. in Met. Eng. A. W. Grosvenor, professor of metallurgy.

Fenn College, Cleveland, Ohio. 4½-yr. cooperative in B. of *Met. Eng. Dr. G. U. Greene, head, Dept. of Metallurgical and Chemical Engineering.

Georgia Institute of Technology, Atlanta, Ga. 4-yr. B. of *Cer. Eng. Lane Mitchell, director, School of Ceramic Engineering.

Harvard University, Cambridge, Mass. Undergraduate instruction in engineering sciences and applied physics, or geological sciences, preparatory to professional study in Graduate School of Engineering in (1) *Physical Met., or in Division of Geological Sciences of the Graduate School of Arts and Sciences in (2) Min. Geol., (3) Pet. Geol., (4) Geophysics; or in the Dept. of Engineering Sciences and Applied Physics of the Graduate School of Arts and Sciences. Marland P. Billings, chairman, Division of Geological Sciences.

University of Idaho, Moscow, Idaho. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) Geol., (4) *Geol. Eng. A. W. Fahrenwald, dean, School of Mines.

Illinois Institute of Technology, Chicago 16, Ill. 4-yr. B.S. in Met. Eng. Otto Zmeskal, director, Dept. of Metallurgical Engineering.

University of Illinois, Urbana, Ill. 4-yr. B.S. in: (1) *Cer. Eng., (2) *Met. Eng., (3) *Mng. Eng. H. L. Walker, head, Dept. of Mining and Metallurgical Engineering; A. I. Andrews, head, Dept. of Ceramic Engineering; George W. White, head of Dept. of Geology.

Iowa State College, Ames, Iowa. 4-yr. B.S. in (1) *Cer. Eng., (2) Mng. Eng. G. L. Bridger, head, Dept. of Chemical and Mining Engineering; C. M. Dodd, head, Dept. of Ceramic Engineering.

University of Kansas, Lawrence, Kans. 4-yr. B.S. in: (1) Geol. Eng., (2) Met. Eng., (3) *Min. Eng., (4) Pet. Eng. R. M. Dreyer, Chm., Dept. of Geol. & Geological Eng.; K. E. Rose, Chm., Dept. of Mng. & Met. Eng.; and C. F. Weinaug, Chm., Dept. of Pet. Eng.

University of Kentucky, Lexington, Ky. 4-yr. B.S. in: (1) *Met. Eng., (2) Mng. Eng. C. S. Crouse, head, Dept. of Mining and Metallurgical Engineering.

Lafayette College, Easton, Pa. 4-yr. B.S. in: (1) *Met. Eng., (2) *Mng. Eng. W. B. Plank, head, Dept. of Mining and Metallurgical Engineering.

Lehigh University, Bethlehem, Pa. 4-yr. B.S. in: (1) *Mng. Eng., (2) Mng. Eng., Eng. Geophysics option, (3) *Met. Eng. A. C. Callen, head, Dept. of Mining Engineering: Gilbert E. Doan, head, Dept. of Metallurgical Engineering.

Louisiana Polytechnic Institute, Ruston, La. 4-yr. curriculum in Pet. Eng. Roy T. Sessums, dean, School of Engineering.

Louisiana State University, Baton Rouge, La. 4-yr. B.S. in: (1) *Pet. Eng., (2) Pet. Geol. Henry V. Howe, director, School of Geology.

Massachusetts Institute of Technology, Cambridge, Mass. 4-yr. S.B. in *Metallurgy. John Chipman, head, Dept. of Metallurgy.

Michigan College of Mining and Technology, Houghton, Mich. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) Geol. Eng. Grover C. Dillman, president.

Michigan State College, East Lansing, Mich. 4-yr. B.S. in Met. Eng. L. G. Miller, dean of Engr.; R. L. Sweet, Chm., Met. Eng.

University of Michigan, Ann Arbor, Mich. 4-yr. B.S.E. *(Met.). George G. Brown, chairman, Dept. of Chemical and Metallurgical Engineering.

University of Minnesota, Minneapolis, Minn. 5-yr. (1) *B. Mng. Eng., (2) B. Geol. Eng., (3) *B. Pet. Eng., (4) *B. Met. Eng. T. L. Joseph, dean, School of Mines and Metallurgy.

Missouri School of Mines and Metallurgy, Rolla, Mo. 4-yr. B.S. in: (1) *Mng. Eng. with options in (a) Mng. Geol., (b) *Pet. Production; (2) *Met., (3) *Cer. Eng., (4) B.S., with major in Geol., Cer., or Met. B.S. in Chemical Eng. for those specializing in Pet. Refining. Curtis L. Wilson, dean.

Montana School of Mines, Butte, Mont. 4-yr. B. S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) *Geol. Eng., (4) Pet. Eng. Francis A. Thomson, president.

University of Nevada, Reno, Nev. 4-yr. B.S. in: (1) *Mng. Eng. (2) Met. Eng. (3) Geol. Eng. Jay A. Carpenter, director, Mackay School of Mines.

New Mexico School of Mines, Socorro, New Mex., 4-yr. B.S. in: (1) *Mng. Eng., (2) Met. Eng., (3) *Pet. Eng., (4) *Geol. Eng., (5) Geophysics, (6) Chemistry. 5-yr. B.E. in: (1) Geology. E. J. Workman, president.

New York State College of Ceramics, Alfred, N. Y. 4-yr. B.S. in: (1) *General Cer. Tech. and Eng., (2) Glass Tech. J. F. McMahon, Acting Dean.

North Carolina State College of the University of North Carolina, Raleigh, N. C. 4-yr. B. of: (1) *Cer. Eng., (2) Geol. Eng. W. W. Kriegal, professor of ceramic engineering; J. L. Stuckey, professor of geological engineering.

University of North Dakota, Grand Forks, N. Dak. 4-yr. B.S. in *Mng. Eng. L. C. Harrington, Dean, College of Engineering, director, Division of Mines and Mining Experiments.

University of Notre Dame, Notre Dame, Ind. 4-yr. B.S. in *Met. Edward G. Mahin, head, Dept of Metallurgy.

The Ohio State University, Columbus, Ohio, 5-yr. (1) *B. Eng. in Mng. with option in Pet. Eng., (2) B. *Cer. Eng., option in Glass Technology, (3) B. *Met. Eng. H. F. Nold, professor of mine engineering; J. L. Carruthers, head, Dept. of Ceramic Engineering; Mars G. Fontana, head, Dept. of Metallurgy; E. V. O'Rourke, professor of petroleum engineering.

University of Oklahoma, Norman, Okla. 4-yr. B. S. in: (1) Geol. Eng., (2) *Pet. Eng., (3) Natural Gas Eng. W. H. Carson, dean, College of Engineering.

Oregon State College, Corvallis, Oreg. 4-yr. B.S. in Mng. Eng., with options in (1) Mng. Eng., (2) Met. Eng. W. E. Caldwell, professor of mining engineering.

Pennsylvania State College, State College, Pa. 4-yr. B.S. in: (1) Geol. & Mineralogy, (2) Geophysics & Geochemistry, (3) Meteorology, (4) Geography, (5) Mineral Eco., (6) *Mng. Eng., (7) Mineral Preparation Eng., (8) *Pet. & Nat. Gas Eng., (9) Fuel Tech., (10) *Met., (11) *Ceramics, Edward Steidle, dean, School of Mineral Industries.

University of Pennsylvania, Philadelphia 4, Pa. 4-yr. B.S. in Met. Eng. R. M. Brick, director, Dept. of Metallurgy.

University of Pittsburgh, Pittsburgh, Pa. 4-yr. B.S. in: (1) *Mng., (2) *Met. Eng., (3) *Pet. Eng., (4) Geol. Eng. E. A. Holbrook, dean, Schools of Engineering and Mines.

Princeton University, Princeton, N. J. 4-yr. Geol. Eng., with degree B.S. in Eng. Kenneth H. Condit, dean, School of Engineering; W. T. Thom, Jr., chairman, Dept. of Geological Engineering.

Purdue University, West Lafayette, Ind. 4-yr. B.S. in *Met. Eng. G. M. Enos, chairman, Division of Metallurgical Engineering, School of Chemical and Metallurgical Engineering.

Rensselaer Polytechnic Institute, Troy, N. Y. 4-yr. B. *Met. Eng. W. F. Hess, head, Dept. of Metallurgical Engineering.

Rutgers University, New Brunswick, N. J. 4-yr. B.S. in Cer. John H. Koenig, director, Dept. of Ceramics.

South Dakota School of Mines and Technology, Rapid City, S. Dak. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) Geol. Eng. Warren E. Wilson, president.

University of Southern California, Los Angeles, Calif. 4-yr. B.S. in: *Pet. Eng. C. R. Dodson, head, Pet. Eng. Dept., Thomas Clements, head, Dept. of Geology.

Stanford University, Stanford, Calif. 4-yr. B.S. in *Min. Sciences. A. I. Levorsen, dean, School of Mineral Sciences.

Agricultural and Mechanical College of Texas, College Station, Texas. 4-yr. B.S. in *Pet. Eng. Also 5-yr. (1)* B. Pet. Eng., with options in: (a) Production, (b) Geol., (2) *B.S. in Pet. Eng. and Mech. Eng., (3) *B.S. in Pet. Eng. and Geol. Eng. Harold Vance, head, Dept. of Petroleum Engineering.

University of Texas, Austin, Texas. 4-yr. B.S. in *Pet. Eng. H. H. Power, chairman, Dept. of Petroleum Engineering.

University of Texas, College of Mines and Metallurgy, El Paso, Texas. 4-yr. B. S. in Mng. Eng. with options in: (1) *Mng. Eng., (2) Met., (3) *Mng. Geol. Wilson H. Elkins, president; E. M. Thomas, dean of Engineering.

University of Tulsa, Tulsa, Okla. 4-yr. B.S. in: (1) *Pet. Production Eng., (2) *Pet. Refining, (3) Pet. Geol., (4) Geophysical Eng. R. L. Langenheim, dean, College of Petroleum Sciences & Engineering.

University of Utah, Salt Lake City, Utah. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) Geol. Eng. C. J. Christensen, dean, School of Mineral Industries.

Virginia Polytechnic Institute, Blacksburg, Va. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) Geol., (4) *Cer. Eng. E. B. Norris, dean of Engineering.

State College of Washington, Pullman, Wash. 4-yr. B.S. in: (1) Geol., (2) *Mng., (3) *Met. Donald L. Masson, acting director, School of Mines.

University of Washington, Seattle, Wash. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng., (3) *Cer. Eng. Drury A. Pifer, director, School of Mineral Engineering.

Washington University, St. Louis, Mo. 4-yr. B.S. in *Geol. Eng. Lawrence E. Stout, dean, School of Engineering.

West Virginia University, Morgantown, W. Va. 4-yr. B.S. in Mng. Eng., with options in: (1) *Mng. Eng., (2) Oil and Gas Eng. G. R. Spindler, director, School of Mines.

West Virginia Institute of Technology, Montgomery, W. Va. 5-yr. B.S. in Mng. on co-operative system in coal. Edward L. Holt, head, Dept. of Mng. and Geology.

University of Wisconsin, Madison, Wis. 4-yr. B.S. in: (1) *Mng. Eng., (2) *Met. Eng. Geo. J. Barker, chairman, Dept. of Mining and Metallurgy.

Yale University, New Haven, Conn. 4-yr. B. Eng. in *Met. C. H. Mathewson, chairman, Dept. of Metallurgy.

CANADA

University of Alberta, Edmonton, Alta. 4-yr. B.S. in Mng. Eng., with options in: (1) Metal Mng., (2) Coal Mng. K. A. Clark, professor of metallurgy; E. O. Lilge, professor of ore dressing; T. H. Patching, asst. prof. of Mng. Eng.

University of British Columbia, Vancouver, B. C. 5-yr. B. of Applied S. in: (1) Mng. Eng., (2) Met. Eng., (3) Geol. Eng. F. A. Forward, head, Dept. of Mining and Metallurgy; M. Y. Williams, head, Dept. of Geology and Geography.

Laval University, Quebec. 4-yr. B.S. in: (1) Geol., (2) Mng. Eng. (3) Met. G. Letendre, director, Dept. of Mining and Metallurgy.

McGill University, Montreal, P. Q. 4-yr. B. Eng. in: (1) Mng. Eng., (2) Met. Eng. J. J. O'Neill, dean of Engineering.

Ecole Polytechnique (Montreal University), Montreal, P. Q. 5-yr. B. Applied S. in: (1) Mng. Eng. and Geol., (2) Met. Eng. P. Mauffette, head, Dept. of Mining and Geology. L. Bourgoin, head, Dept. of Metallurgy.

Nova Scotia Technical College, Halifax, N. S. 5-yr. B. Eng. in Mng. Eng. A. E. Flynn, professor of mining engineering.

Queen's University, Kingston, Ont. 4-yr. B.S. in: (1) Mng. Eng., (2) Met. Eng., (3) Economic Geol. A. V. Corlett, head, Dept. of Mining Engineering; T. V. Lord, head, Dept. of Metallurgical Engineering; E. L. Bruce, head, Dept. of Geology.

University of Toronto, Toronto, Ont. 4-yr. B. Applied S.: (1) Mng. Eng., (2) Met. Eng., (3) Mng. Geol. R. E. Barrett, professor of mining engineering; L. M. Pidgeon, professor of metallurgical engineering; E. S. Moore, head, Dept. of Geological Sciences.

Board Acts on Publications at June Meeting

Meeting on June 15, the AIME Board of Directors, with President Young presiding, accepted with much satisfaction the report of the tellers in the recent dues referendum, as published in the July journals. Amendment of the Bylaws effecting the increase will be voted at a Board meeting on July 27. Also, the report of the Nominating Committee, nominating Donald H. McLaughlin as President in 1950, was accepted. The names of the nominees were published last month. The Board named Gail F. Moulton as the ninth candidate for Director, inasmuch as otherwise the Petroleum Branch would have no representative in the New York metropolitan area. Candidates for Divisional offices, as printed in the July journals, were announced except that R. W. French is named as a Vice-Chairman of the Petroleum Division instead of a member of the Executive Committee.

Prices were set, on the basis of orders so far received and expected future sales, for the three volumes of Transactions to be issued early in 1950, consisting of the material in the Transactions sections (Section 3) of the journals in 1949. An opportunity was provided on the 1949 dues bill and selection slip for ordering these volumes, and further copies will be available as long as the supply lasts. The price will be $3.50 to members including Student Associates for a first copy of any or all of the three volumes; additional copies will be billed at the nonmember price of $7 each. These volumes will be known as "Transactions, AIME, 1949," thus duplicating in date the volumes authorized for publication this year, but the volume numbers will be different and it is thought that in future it will be desirable to have the volumes carry the date of publication in the journal.

The three journals will be available next year on the same basis as in 1949: one free subscription to one journal as part consideration of dues, with one subscription to either or both of the other journals at $4 each. Additional subscriptions to one journal will be billed at the nonmember subscription price of $8 per year, or $9 to foreign countries outside of the Americas.

Authorization was voted to follow the recommendation of the Seeley W. Mudd Memorial Fund Committee to send to all new Junior Members who have not received any of the Mudd books, and to future new Junior Members, one copy each of "Seventy-five Years of Progress in the Mineral Industry" (75th AIME Anniversary volume), and "A Professional Guide for Junior Engineers," by William E. Wickenden, recently published by the Engineers Council for Professional Development. Also, any one of the following volumes will be supplied free on request: "Modern Uses of Nonferrous Metals," "75 Years of Progress in Iron and Steel," "A Brief History of the Science of Metals," and "Coal Through the Ages."

Other recommendations of the Mudd Committee accepted included: (1) Building up the "AIME Series" to twelve or fifteen volumes, including one of specific interest to each of the professional Divisions of the Institute. (2) Promoting the sale of the volumes through increased publicity. (3) Printing of 3000 copies of the revised edition of "Coal Preparation," to be sold to members and Student Associates at $4 for a first copy, $8 to nonmembers and for additional copies to members, and $6 in lots of ten or more. (4) R. Dawson Hall to be editor of the previously authorized volume on health and safety in mining.

At the Annual Meeting in San Francisco, the resignation of the H. W. Johnson Committee, appointed more than a year earlier and whose report had been made at the Annual Meeting in 1948, was received. The Board had been loath to accept it, and the matter had been discussed at successive Board meetings this spring. The Committee had been especially invited to appear before the Board at its June meeting to discuss the progress so far made in adopting the Committee's recommendations. Mr. Johnson and Messrs. Leighton and Ball, however, felt that the resignation should stand, so it was accepted, with full appreciation of the excellent report that the Committee had made, on which the recent and present reorganization of the Institute structure, practice, publication policies, and personnel has been based.

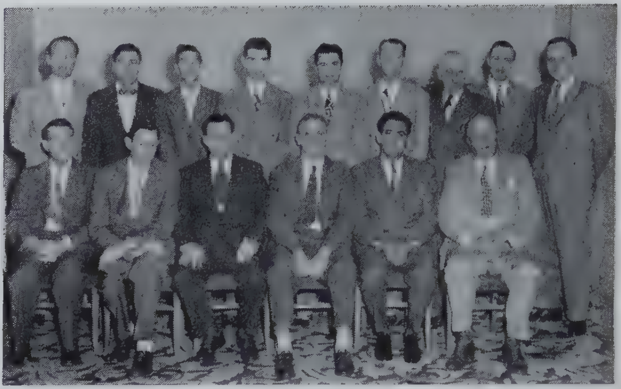
In the effort to reduce costs of Institute operation, and to improve its service, Mr. Head gave a progress report on plans to survey the office procedure of the AIME and the other Founder Societies; Mr. Beall gave data on possible savings that might result from splitting the personals into Section 1 of the appropriate journals; and Mr. Appleton reported on an investigation of the possibility of reducing printing costs. It was voted to continue publication of the personals in the All-Institute section for the rest of 1949.

Selection of Francis H. Brownell as Rand Medalist for 1950 was approved. Gail F. Moulton was appointed to serve out Mr. Roosevelt's term as representative on United Engineering Trustees. AIME representatives at the First Pan-American Engineering Congress in Rio de Janeiro, July 15-24, were named as follows: Fred T. Agthe, W. H. Carson, John H. Evans, Sherwin F. Kelly, and Henrique Capper Alves de Souza. Additional representatives at the Empire Mining and Metallurgical Congress in Great Britain, July 9-23, were named as follows: P. J. Cutting and W. E. Wrather. William J. Coulter and Lloyd E. Elkins were named as representatives at the 75th anniversary celebration of the Colorado School of Mines, Sept. 29 to Oct. 1. New Affiliated Student Societies were recognized at the University of Pennsylvania—the Metallurgical Engineering Society, and at Penn State—the Petroleum Engineering Society. Progress was reported in organizing the Mining, Geology, and Geophysics Division of the AIME, with the assistance of E. R. Borcherdt.

Directors present included: Messrs. Young, Bowles, Daveler, Head, Kinzel, Kraft, Millikan, Pehrson, Rhines, Schumacher, Sullivan, Suman, Swainson, Swift, Wrather, and Fletcher, with H. P. Greenwald as alternate for N. G. Alford. The meeting, which adjourned at 4:10 p.m., was preceded by an informal luncheon at 12:30.

Mid-Year Meeting . . .

Committeemen for the Mid-Year Meeting pose, with Scott, Faust, Mueller, Johnson, Nekervis, and MacQuigg in the front row, and Westerman, Anderson, Bowers, Pfoor, Melvin, Snavely, and Deubner backing them up.



They wouldn't fit in one picture, so seated are: O'Rourke, Bowen, Reilly, Jones, Spretnak, Salsich; and standing: Hatch, Greenidge, MacIntosh, Cunningham, Woodward, Pilcher, Reed, Alkire, and Advent.

More Important Sessions

Reports are still coming in from Division Chairmen and committee heads regarding plans for the Mid-Year Meeting to be held in Columbus, Ohio, from September 25-28. A detailed program will be printed in the September issues of the Institute Journals.

industrial pollution session

Recognizing the increasing importance of air pollution problems, especially as related to the mineral industries, the Coal Division's Program Committee has scheduled an afternoon of discussion of the topic for Wednesday, Sept. 28. Elmer Kaiser, Committee Chairman, has announced that four nationally known authorities will address the symposium.

L. C. McCabe, formerly with Los Angeles County, and now with the Bureau of Mines in Washington, will discuss "Air Pollution by Industrial Gases and Liquids," and T. C. Wurts will present a paper on the "Air Polluting Solids of Allegheny County, Pa." Allegheny Co., in May, adopted new air pollution regulations, evolved by industry itself, to help cope with the local problem. Discussion will be conducted by H. F. Hebley, of the Pittsburgh Consolidated Coal Co., well-known as a pioneer in anti-pollution work, and W. C. L. Hemeon, noted authority with the Industrial Hygiene Foundation.

Members are urged to attend this very timely and important session.

The Women's Committee affairs are handled by Mesdames MacIntosh, Kaiser, Burnhagen, Anderson; back row, Mesdames Mueller, Elsea, Pilcher, Scott, and Manning.

students urged to attend forum

Another lively student forum will be held during the Mid-Year Meeting. Armed with experience gleaned from forums at El Paso and San Francisco, the young men will face prospective employers in what promises to be a highly informative session.

Industrial leaders are prepared to answer a lot of questions from this year's crop of graduates and students, especially in view of the dearth of jobs available these days. C. E. Bales, vice-president of the Ironton Fire Brick Co.; M. D. Cooper, vocational training manager, National Coal Assn.; and James Hyslop, executive vice-president, Hanna Coal Co., will be among those attending. Person-to-person contact with employers, plus a closeup view of AIME activities, will prove valuable to students. A special student rate for attending the meeting is expected.

Students are urged to seek out plane, train, bus, and hitch-hiking schedules before September. *Professors will please contact their students now, and urge their attendance.*

. . . Columbus, Ohio, September 25 to 28

The Drift of Things

. . . as followed by EDWARD H. ROBIE

More Government Control Threatened

Many officials of companies engaged in the extraction of our country's mineral wealth are alarmed at the implications of an extension of authority assumed by the Federal Power Commission toward the producing, gathering, and marketing functions of the natural gas industry. For years the majority opinion of the Commission has been that it had no powers under the Natural Gas Act of 1938 to regulate production, but one of the five Commissioners has recently altered his point of view. To clarify the Commission's authority, and to maintain the attitude heretofore taken, bills known as the Lyle and Harris bills have been introduced into the House, and more recently Bill No. 1498 has been introduced into the Senate by Senator Kerr, of Oklahoma, on behalf of himself and Senator Thomas, also of Oklahoma.

If peacetime natural gas production and its sales can be controlled by the Federal Power Commission, then it is argued that all mineral resources could likewise be controlled, which is the occasion of the present alarm by some of the mining group.

We have asked one more conversant with the situation than are we to prepare a statement which we are glad to quote as follows:

"Americans who believe that private development of our mineral resources will continue to produce the greatest benefits for the country should be interested in legislation introduced in the 81st Congress. The proposed law, known as the "Kerr Natural Gas Bill," would amend the Natural Gas Act of 1938 by more clearly defining the powers of the Federal Power Commission over the production and gathering of natural gas.

"Briefly, the National Gas Act of 1938 gave the Federal Power Commission power to regulate *interstate* transportation of natural gas and its sale in *interstate* commerce for resale. The Act did *not* grant power to regulate production or gathering. In turn this was long believed to exclude power to regulate the prices charged by producers and gatherers.

"In recent years, however, the jurisdiction of the Commission has gradually been extended, until now a majority of the Commission's members assert that it should have full control over the prices charged by producers and gatherers of natural gas.

"What does this mean? In operations over which it has jurisdiction, the Commission never allows, under court-approved principles, a return greater than 6½ per cent of the original cost of the properties involved. This rule, if applied to an oil field which produces both oil and gas—and that includes most oil fields in this country—could prevent any return at all from the production of casinghead gas, if the producer has already received the allowed return from his oil production. Furthermore, in the case of a purely gas-producing field, returns from the sale of gas might be zero if the producer had already recovered the original cost of his property. Also, since the base figure on which a fixed return is allowed is the original cost of a property, no allowance is made for the enhanced value of properties due to new discoveries.

"Under such circumstances it is obvious that the inducements for a property owner to invest in facilities for the production and gathering of natural gas are seriously impaired.

"The Kerr Natural Gas Bill, realizing that Federal regulation of the prices at which natural gas may be sold in the field by producers and gatherers would inhibit the development of this natural resource, and therefore is against the public interest, specifically prohibits such price regulation. Because of the diversity of opinion as to the powers granted by the 1938 Act, such clarification seems desirable.

"The Federal Power Commission has also claimed for itself the power to control the uses to which natural gas shall be put, and to prohibit the sale of natural gas in competition with other fuels in certain areas. It would seem, however, that the end use of any product should be governed by prices, utility, and the desires of the purchaser, and not by government edict.

"Except in time of war, it is not the function of government to control the end use of natural gas any more than it is its function to control the use of lumber, corn, or cotton; coal, lead, or iron. Certainly control over the end use of one commodity could lead to control over the end use of others.

"Eventually, unless restricted by the Kerr Natural Gas Bill or similar legislation, the Federal Power Commission could extend its jurisdiction so as to drive private enterprise out of the natural gas business. Once that is accomplished, it would be a short step to Government control of oil, coal, copper, and other natural resources—with Federal ownership or state socialism as an ultimate result.

"The bill now pending would merely amend the Natural Gas Act of 1938 to limit the Federal Power Commission to the powers originally thought to be conferred upon it.

"It is entirely appropriate for members of the AIME to advise their Senators and Representatives about their views and wishes on this subject."

Jobs Wanted

Our available space is again confined to one page this month, but we do want to get in a word about the plight of the June engineering graduates. Over 1200 of them have registered with the Engineering Societies Personnel Service for jobs as this is written. Of these, 105 are chemicals, 100 civils, 345 electricals, 625 mechanicals, 55 mining and metallurgical, and 40 geology and physics. The Service has approached many large potential employers but is receiving only two or three requests a week for men.

If an employer who reads this can possibly place one of these budding engineers, even if a less well-trained man must be displaced in the process, the investment should prove a good one. Give a man a job, train him, and have him ready when you need him.

File of Key Engineering Personnel Object of EJC Questionnaire

To provide source material for a who's who in engineering research, development, and other scientific operations for use by the National Military Establishment, the Engineers Joint Council acting through The American Society of Mechanical Engineers has accepted the task of providing the Office of Naval Research with the names, addresses, ages, and details of professional and scientific qualifications of 100,000 key engineers in all branches of American engineering.

The source file of key engineering personnel thus obtained will provide a valuable tool for solving a variety of technical personnel problems. Its use will diminish disturbances of the national economy, organization of industry, and the personal welfare of engineers, and provide a means by which national resources of technical personnel can be ascertained. The file will also point up weak spots which should be strengthened by education, training, and other means. As a national asset the body of facts will be available to private industrial, educational, and professional-society planning groups, and for other legitimate purposes.

A four-page questionnaire has been mailed to 100,000 engineers holding the grade of member or higher in eighteeen national professional engineering societies. The returns will be collected by the ASME and turned over to the Office of Naval Research of the National Military Establishment for classification.

The project is the result of a conference held in Washington, D. C., last fall attended by EJC representatives and many other engineering agencies, at which was discussed the need for a list of 25,000 key engineers working in research, development, and other scientific projects who could be called in on a full or part-time basis to work on the broad scientific programs of the National Military Establishment. The task of collecting personal and professional data fell to the EJC as the largest joint agency of the engineering profession. ASME assumed administration of the project as contracting agent of the EJC.

The Engineers Joint Council points out that this is not just another questionnaire, but one sent to engineers selected from the upper echelon of the profession. The data sought is not intended for general government use but will go directly to the engineering agencies of the National Military Establishment, who will make direct use of it. As the questionnaire will provide the key to opportunity to professional and patriotic service, engineers selected to receive it are urged to give it serious attention and to answer all questions fully.

Calendar of Coming Meetings

AUGUST

- **4 Reno Branch, Nevada Section, AIME.**
- **10 El Paso Metals Section, AIME.**
- **16 Gulf Coast Section, AIME.**
- **22 Alaska Section, AIME.**

SEPTEMBER

- 25-28 American Mining Congress, Metal Mining Convention, Hotel Davenport, Spokane, Wash.
- **25-28 Mid-year Meeting, AIME, Neil House, Columbus, Ohio.**
- 29-30 ASME, fall meeting, Erie, Pa.
- 29-Oct. 1 Colorado School of Mines, 75th anniversary celebration.
- **Sept. 30-Oct. 1 Southern Ohio Section of Open Hearth Committee, AIME, fall meeting, Deshler-Wallick Hotel, Columbus.**

OCTOBER

- 3-4 National Assoc. of Corrosion Engineers, Adolphus Hotel, Dallas.
- **5-7 Petroleum Branch, AIME, fall meeting, Plaza Hotel, San Antonio, Texas.**
- 13-14 Texas Mid-Continent Oil and Gas Association, annual meeting, Rice Hotel, Houston.
- **14 Eastern Section, Open Hearth Committee, Iron and Steel Division, annual all-day fall meeting, Warwick Hotel, Philadelphia.**
- **14 Southwestern Section, Open Hearth Committee, Iron and Steel Division, Kansas City, Mo.**
- **17-19 Institute of Metals Division, AIME, fall meeting, Allerton Hotel, Cleveland.**
- 17-21 National Metal Congress and National Metal Exposition, Public Auditorium, Cleveland, Ohio.
- 17-21 American Society for Metals, annual meeting, Cleveland, Ohio.
- 17-21 American Welding Society, annual meeting, Cleveland, Ohio.
- 17-23 AIEE, 1949 Mid-West meeting, Netherland Plaza, Cincinnati.
- 19-20 Society for Non-Destructive Testing, Cleveland, Ohio.
- **20-21 Petroleum Branch, AIME, Elks Club, Los Angeles.**
- 24-28 Thirty-seventh National Safety Congress and Exposition, Chicago.
- **26-27 Joint Fuels Conference, ASME-AIME, French Lick Springs Hotel, French Lick, Ind.**
- **28 Pittsburgh Section of Open Hearth Committee and Pittsburgh Section, AIME, annual fall meeting, William Penn Hotel, Pittsburgh.**
- 28-29 ECPD, annual meeting, Edgewater Beach Hotel, Chicago.

NOVEMBER

- 1-5 Pacific Chemical Exposition, California Section, American Chemical Society, San Francisco Civic Auditorium.
- 2-4 American Society of Civil Engineers, fall meeting, Washington, D. C.
- 7-10 AIChE, annual meeting, Pittsburgh, Pa.
- 7-12 International congress on tunnel driving in rock formation, organized by the Societe de l'Industrie Minerale. Information on meeting available from French Mining Mission, 1322 18th St., N. W., Washington, D. C.
- **9-11 Industrial Minerals Division, AIME, Tampa, Fla.**
- 10-14 ASTM, first Pacific area national meeting, San Francisco, Calif.
- 12-14 Geological Society of America, annual meeting, Hotel Cortez, El Paso.
- 16-18 Industrial Hygiene Foundation, 14th annual meeting, Mellon Institute, Pittsburgh.

DECEMBER

- 7 American Mining Congress, Annual Business Meeting, New York City.
- **8-10 Seventh Annual Conference, Electric Furnace Steel Committee, Iron and Steel Division, AIME, Hotel William Penn, Pittsburgh.**

JANUARY 1950

- 18-20 American Society of Civil Engineers, annual meeting, New York.
- 30 AIEE, winter meeting, New York.

Do Not Send Cash to the AIME

Occasionally members send small amount of cash to the Institute in payment for publications, and sometimes even pay their dues with five and ten dollar bills. Ordinarily such sums arrive safely, and are properly credited, but occasionally such remittances are never received. The Institute wishes again to emphasize that it cannot be responsible in such instances, and urges members to use checks or money orders even for small amounts.

Approaching Prospects for Membership

Among the duties and privileges of all AIME members interested in building up their professional society is the securing of new members. If every member would hold himself responsible for securing just one new member, the growth and prosperity of the AIME would show a startling upturn. Application blanks will gladly be forwarded on receipt of a postal card request. Many blanks are now outstanding, and it should be made clear, in approaching prospects, that the dues for the next three years will be $5 higher for Members and Associate Members, and $2 higher for Junior Members, than is stated on the application blanks.

News of AIME Members

Lew Adamec is at present section superintendent of Cie. Aramayo de Mines en Bolivie, Casilla 674, La Paz, Bolivia. He previously held the post of level foreman for the Braden Copper Co. at Rancagua, Chile.

D. L. Anderson is now addressed at Empresa Minera de Nicaragua, Apartado 195, Managua, Nicaragua.

George Ross Bancroft, Canadian consulting mining engineer, has now changed his address from Vancouver, B. C., to Okanagan Mission, B. C., which will be his future home and address.

Ralph C. Beerbower and **Ralph C. Beerbower, Jr.,** father and son, appeared in the July News all mixed up; the fault was ours. Mr. Beerbower, Sr., is district manager of the Goodman Mfg. Co. Mr. Beerbower, Jr., after graduating from Penn State in 1948, joined the H. C. Frick Coke Co. and was recently assigned to the post of assistant to the superintendent at Leisenring No. 3 Mine, West Leisenring, Pa. We apologize to both gentlemen.

Arthur H. Bunker

Arthur H. Bunker resigned as a general partner of Lehman Brothers on June 30 to become president of the Climax Molybdenum Co. At present a director of the American Metal Co., the Firth Steel and Carbide Corp., and Climax Molybdenum, Mr. Bunker was the founder in 1923 and first president of the U. S. Vanadium Corp. During the recent war he served with the OPM and WPB, becoming chief of staff of the latter.

T. W. Lippert

T. W. Lippert has been appointed manager of publications by the AIME. In this capacity he will also act as editor of the *Journal of Metals.* Mr. Lippert is a graduate of Carnegie Institute of Technology, with a B.S. and M.S. in physics, and for the past sixteen years has been associated with *Iron Age,* serving in latter years as directing editor of that publication, and as a director of the parent Chilton Co.

J. W. Bostick plans to remain at 6028 Folsom Drive, La Jolla, Calif., until next November. His office is still at 3116 Main St., Dallas, Texas, where mail or calls are promptly forwarded by his secretary. Being a University of California man, he has met many old friends and college mates there, in Los Angeles, and in San Francisco.

Arthur E. Buller, who was formerly resident geologist for the Kelowna Exploration Co. at the Nickel Plate Mine, Hedley, B. C., has accepted the post of chief geologist for the Pend Oreille Mines and Metals Co. at Metaline Falls, Wash.

R. W. Crosby is on the staff of the Benguet Consolidated Mining Co., Baguio, P. I. He was previously employed by Marsman and Co. in Manila.

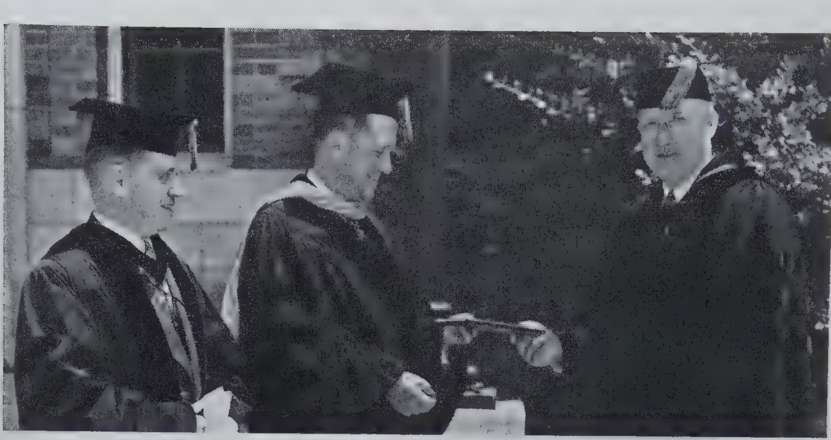
Douglas MacDonald Dunbar, who had been in Chuquicamata with the Chile Exploration Co., has been made assistant to the executive vice-president of that Company. He is now at Company headquarters located at 25 Broadway, New York City 4.

Howells Frechette has been elected vice-president of the American Ceramic Society. Former chief of the industrial minerals division of the Bureau of Mines, Ottawa, he is the first Canadian to hold this post.

Cy W. Greenhalgh, who was research metallurgist for the Remington Arms Co., Bridgeport, Conn., has recently joined the staff of the Old Town Co., in Old Town, Maine, as general manager. He resides at 144 College Rd., Orono.

Jean McCallum retired on May 1 from his service with the National Lead Co., completing a period of almost exactly 31 years. He became connected with National as assistant superintendent of the River Smelting and Refining Co., Florence, Colo., in 1918, where he handled all phases of the operation and assisted in perfecting the metallurgy at many points. When this plant ceased operations, he was transferred to Collinsville, Ill., as superintendent of the lead smelter of the St. Louis Smelting and Refining Co., from which point he moved to St. Louis as research and development metallurgist for the National Lead branch and Titanium Division. Following five years as plant superintendent of the whitelead and oxide plant, he was made vice-president of the St. Louis Smelting and Refining Co. and manager of the St. Louis Smelting and Refining Works, division of National Lead, which post he held until his retirement. In 1947 he was also made general manager of the Texas Mining and Smelting Division at Laredo, Texas.

Jean McCallum



Curtis L. Wilson, dean of the School of Mines and Metallurgy, University of Missouri, watches Andrew Fletcher receive an honorary degree of Doctor of Engineering from F. A. Middlebush, president of the University, at the commencement exercises in Rolla, at which Dr. Fletcher delivered the address.

Paul W. Fairchild received an M.S. degree in geology from the University of Kansas in February and is now employed as a junior geologist with the Shell Oil Co. exploration department in a one-year training program.

E. W. Hunt has been appointed superintendent of mines with the Hudson Bay Mining and Smelting Co., Flin Flon, Man.

E. J. Carlyle

E. J. Carlyle officially retires as executive director and secretary-treasurer of the Canadian Institute of Mining and Metallurgy on Sept. 30. He was born in Woodstock, Ont., in 1877 and graduated in mining engineering in 1904 from McGill University. Upon graduation, he received early professional training at Anaconda, Mont., and Arizona. He held various important posts in several foreign countries, as well as Canada, such as for the Sissert Corp. in Russia for whom he designed a smelter and refinery at Salt Lake City. Before his appointment as secretary-treasurer of the Canadian Institute in 1931, he was superintendent of the American Smelting and Refining Co. in Peru. He was made executive director and secretary-treasurer in January 1947.

L. H. Lange, vice-president and consulting metallurgist of the Galigher Co., Salt Lake City, sailed with his wife from New York City on June 15 on the "Robin Hood" for Southwest Africa where he plans to spend several months at Tsumeb. After leaving Tsumeb, time will be spent visiting Johannesburg and the copper properties in Northern Rhodesia before returning to the States.

Geoffrey B. Leech, who had been attending Princeton University, is now working for the Geological Survey of Canada, Ottawa, Ont.

William F. Machonis is employed as a service engineer by Combustion Engineering Superheater Inc., Philadelphia, Pa.

Willam B. MacPhee, formerly of the Minerals Engineering Co. of Los Angeles, is at present with the Castrovirreyna Metal Mines Co., Casilla 101, Santa Ines, Huancavelica, Peru.

Howard Maidment, who had been a student at the University of British Columbia, can be reached at the Polaris-Taku Mining Co., Tulsequah, B. C.

Frederic H. Main, upon leaving Columbia University where he was a lecturer in economic geology during the absence of **C. H. Behre, Jr.,** is now on the staff of the Bertha minerals division of the New Jersey Zinc Co. at Austinville, Va.

W. B. Mather, chairman of the division of mineral technology of the Southwest Research Institute, San Antonio, Texas, before June 1 was with the Midwest Research Institute in Kansas City, Mo.

Richard D. Mayne, manager of the Hannibal, Mo., plant of the Universal Atlas Cement Co., a U. S. Steel subsidiary, became manager of the company's plant at Hudson, N. Y., on June 1. A 1930 graduate of Carnegie Institute of Technology, he joined Universal Atlas in Chicago in 1937 as an industrial engineer. After serving the cement company in various capacities he was appointed assistant plant manager at Hannibal in 1943 and three years later became plant manager.

John B. McIntyre, formerly a student at Oregon State College, is at present working for the U. S. National Museum, Room 331, Washington 25, D. C.

John F. Meissner is president of John F. Meissner Engineers, Inc., 308 West Washington St., Chicago 6. He had been associated with Robins Conveyors, Inc., also of Chicago.

William C. Miller, who was a student at the University of California at Berkeley, is at present working as an assistant mining engineer for the Anaconda Copper Co. He can be reached at 615 W. Park, Butte, Mont.

Robert W. Michael, specialist in the design of diamond recovery equipment, is now engaged with the New York Engineering Co. as consulting engineer in the fabrication of the first mechanical diamond washing unit to be installed in the new Venezuelan alluvial fields. The plant will contain many unique mechanical features, and is to be constructed so that it can be demounted for air transport. The flow sheet will include the latest developments in diamond recovery practice. Mr. Michael may be reached in care of the New York Engineering Co., 75 West St., New York 6.

Frank R. Milliken, assistant manager, Titanium Division, of the National Lead Co., can now be reached at 111 Broadway, New York City, having transferred from Tahawus, N. Y.

B. E. Mix has retired as plant engineer of the Utah Copper Co. at Garfield, Utah, and is now residing at 2767 Claybourne Circle, Salt Lake City.

E. S. Moore, head of the department of geological sciences, University of Toronto, and formerly dean of the school of mines, Pennsylvania State College, retired on June 30 with the title Professor Emeritus after 27 years on the staff.

Jack E. Morris, research engineer of the general technical department of Jones & Laughlin Steel Corp., although still in the same department, can now be reached care of the Company, Jones & Laughlin Bldg., 3rd and Ross St., Pittsburgh 20. He had previously been at Star Lake, N. Y.

R. G. K. Morrison is returning to Canada, and on Sept. 1 will take over the duties of professor of mining engineering at McGill University. Mr. Morrison was a director of the Mysore Gold Mining Co., Ltd., and a managing director of John Taylor & Sons (India), Ltd. The latter company, being an off-shoot of the old London firm of John Taylor & Sons, was formed to take over interests in India, including the management of the four operating companies of the Kolar gold field.

Eric A. Rudd, having resigned from the position of chief geologist of the Broken Hill Pty. Co., of Melbourne, Australia, has taken the chair of mining and economic geology at the University of Adelaide. This is the first university department of mining and economic geology in Australia; Professor Rudd hopes that it will become the center for teaching mining geology on that continent from now on. He can be addressed at the University, North Terrace, Adelaide.

William F. Jahn

William F. Jahn recently returned to the United States from Argentina after eight years consulting work in that country and is now enjoying a vacation on his ranch at Stark, Missoula County, Mont.

Frank E. Siegfreid graduated from the Colorado School of Mines in May and is now employed by Telluride Mines Inc., Telluride, Colo.

Robert C. Stanley, chairman and president of the International Nickel Co. of Canada, delivered the address at the spring convocation held on May 21 at Queen's University, Kingston, Ont. He was the recipient of the honorary degree of LL.D. along with **W. B. Timm,** who retired recently as director of mines, forests and scientific services branch, Department of Mines and Resources; and **Stanley N. Graham,** former head of the department of mining at Queen's.

Waters, Kudlich, Otto, James, Reinhardt, backed by Romischer, Oehler, Jenkins, Boyd, McGleerey, Reed, Petzold, and Thomas pose at the Marvine colliery of the Hudson Coal Co., Scranton, Pa., when James Boyd, director of the Bureau of Mines, made his first visit to the anthracite northern coal field. He was taken on a tour by officials of the Glen Alden Coal Co., Lehigh Coal Co., and the Hudson Coal Co. At the evening banquet in Scranton, Dr. Boyd gave a talk on general economics of the metals and minerals of this country.

Blakemore E. Thomas, of the California Institute of Technology, has been appointed assistant professor of geology at the University of Kansas, Lawrence. Dr. Thomas will teach work in petrography and economic geology.

H. W. Thoms, geologist with the Creole Petroleum Corp., Caracas, Venezuela, will be on vacation in the States from July 1 to Aug. 19. His address while here will be 242 Pacific St., Bakersfield, Calif.

Robert E. Tally, Jr., can be reached care of Eastern Mining and Metals Co., Kuala Dungun, Trengganu, Malaya. He had been with Foley Bros., Inc., at Pasadena, Calif.

Robert Van Nostrand has earned his degree of Master of Science in physics at the Missouri School of Mines and is now working for his doctorate in geology at the University of North Carolina.

C. E. Visel, formerly with the Cia. Minera Nacional at Chihuahua, is now on the staff of Negociacion Minera, Sta. Maria de la Paz y Anexas, Matehuala, S.L.P., Mexico.

Dooley P. Wheeler, Jr., geologist, is now with the American Metal Co.; his address is 232 Judge Bldg., Salt Lake City.

Robert A. Willoughby joined the staff of the Yucca Mining and Milling Co., Box 67, Yucca, Ariz. He had been with the Union Sugar Co. at Betteravia, Calif.

William Wraith, Jr., recently changed his job from the Cananea Consolidated Copper Co. in Sonora, Mexico, to the Chile Exploration Co. in Chuquicamata, Chile.

James H. Wren, after covering a number of Central and South American mining examinations, is back in the United States. He has taken the operational consulting account of the Sunshine Gold Mining Company's Redding, Calif., properties, which are about to be put under production. His address is 4317 D St., Sacramento, Calif.

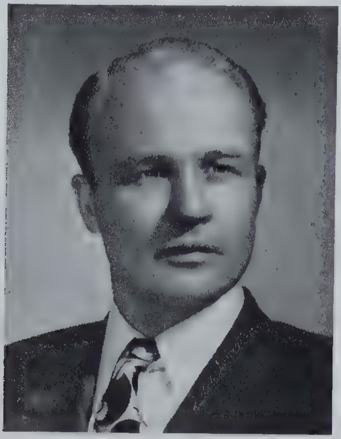
Charles E. Wyndham is now employed as a mining engineer by the Bureau of Mines and can be addressed care of the Bureau, Box L, University, Ala. He previously worked for the Standard Lime and Stone Co., Kimballton, Va.

Harry J. Wolf

Harry J. Wolf, of Behre, Dolbear and Co., was in Mexico recently inspecting mineral deposits in the state of Chihuahua.

• In the Metals Divisions

Glenn L. Allen, previously associated with L. W. Kelley of Park Ridge, Ill., is now employed by the Reynolds Metals Co., 3rd and Grace Sts., Richmond, Va.


Jay W. Fredrickson

Jay W. Fredrickson, formerly at the University of Utah, has joined the staff of the School of Mineral Industries, Pennsylvania State College, as chief of the division of metallurgy.

Samuel E. Atkins, president of the S. E. Atkins Co., has announced the incorporation of Atkins-Walker Co. Offices will continue at 612 Alworth Bldg., Duluth, Minn. Drilling operations which have been carried on for 29 years by S. E. Atkins Co. were turned over to the new company on May 2.

Francis O. Case, former assistant to the vice-president of the Anaconda Copper Mining Co., has been made a vice-president of the Company.

Raf De Bie has finished his studies at Carnegie Tech and received a master's degree. He is touring the country to see something of our industries and will return to Belgium early in August to start working in the research department of the Trefileries Leon Bekaert at Zwevegem.

Robert D. Fitzgerald has taken the job of assistant metallographer with the Aluminum Co. of America at New Kensington, Pa. His home address in New Kensington is 309 Charles Ave.

Arnold W. Greenius is now attached to the department of research and development of the Dominion Steel and Coal Corp. of Sydney, N. S.

Max Hansen has left his associate professorship at the Illinois Institute of Technology to take a position with the Armour Research Foundation which is located on the IIT campus. Members of the AIME Student Chapter at the school presented Dr. Hansen, who was one of the students' favorite instructors, with a going-away present. The professor had come to the U. S. A. but two years ago, and his departure from the IIT faculty is considered as "great loss to both the department and the students."

John C. Kinnear on June 6 delivered the commencement address to 227 graduates of the University of Nevada. Mr. Kinnear, vice-president of the Kennecott Copper Corp. of New York City, was the recipient of an honorary degree of doctor of laws. In addition to his mining activities, he is vice-president of the Nevada Northern Railway and of the Ely National Bank. **Jay A. Carpenter,** director of the Mackay School of Mines of the University of Nevada, was awarded the honorary degree of doctor of science.

Fritz V. Lenel has been made associate professor in the department of metallurgical engineering at Rensselaer Polytechnic Institute. He earned his doctorate at the University of Heidelberg in 1931, and did graduate work at the University of Goettingen until 1933. He joined the Rensselaer staff in 1946 after ten years with the Moraine products division of General Motors.

John W. Axelson

John W. Axelson recently received a Ph.D. degree from the University of Minnesota where he majored in chemical engineering and minored in metallography. He is now employed as a research engineer doing research and development work on metallic gaskets in the research center of the Johns-Manville Corp., Manville, N. J.

Robert F. Mehl, director of the metals research laboratory and head of the metallurgical engineering department at Carnegie Institute of Technology, Pittsburgh, flew to Brazil on June 29 to be a guest for about four weeks of the Research Institute of the State of Sao Paulo at their fiftieth anniversary. Dr. Mehl will also take part in the dedication of new laboratories at the Cidade Universitaria, and will attend the fifth anniversary of the Brazilian Society of Metals, which he helped organize. He lectured in Brazil in 1943 at the request of Nelson A. Rockefeller, co-ordinator of Inter-American Affairs. Dr. Mehl is a permanent member of the faculty of the University of Sao Paulo, from which he received an honorary doctor's degree.

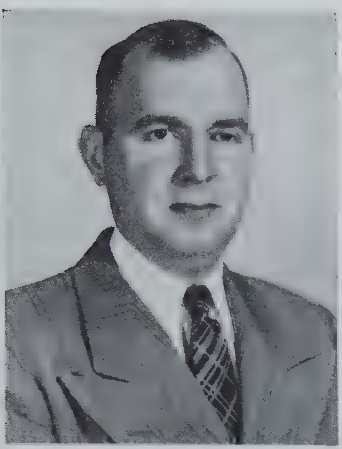
Norman L. Mochel, manager of metallurgical engineering for the Westinghouse Electric Corp., has been elected a member of the board of the American Society for Testing Materials for a three-year term. First employed in the inspection department of the then Westinghouse Machine Co., he later was responsible for the work of testing materials. During the first World War he served overseas in the Corps of Engineers. For many years he has been in his present position, an authority on the materials going into the turbine and other forms of power generation.

George F. Newton is a trainee with the Steel Co. of Canada, Hamilton, Ont. His mail goes to 1077½ Beach Blvd., Hamilton.

Antonio C. Oliveira is now assistant engineer of the foundry department of Laminacão Nacional de Metais, and his mailing address is Rua Heliotropos, 245 (Vila Mariana), São Paulo, Brazil. He had been associated with the Cia. Siderurgica Nacional at Volta Redonda.

Bruce Pierce was married to Helen Decker on June 18 at a ceremony at the Metropolitan Methodist Church in Washington, D. C. The groom, who is in the ordnance department of the regular army as Lieutenant Colonel, is at present taking a two-year graduate course in engineering at Cornell University. The bride is a native of Washington, D. C., and a graduate of Wilson Teachers College. The couple will reside at R. D. 4, Ithaca, N. Y.

Adolph O. Schaefer, assistant to the executive vice-president of the Midvale Co. of Philadelphia, has been appointed to the research committee of Franklin Institute. A native of Pennsylvania, residing in Broad Ax, Pa., he graduated from the University of Pennsylvania in 1922 with a B.S. in chemical engineering. He joined Midvale as a research assistant shortly after graduation and became engineer of tests in 1937 and executive metallurgical engineer in 1944. He held many important posts during the last war, one of which was that of chairman of the gun development group in the Metallurgical Advisory Board.



Howard Peters

Howard Peters was appointed as project engineer for the rollpin division of the Elastic Stop Nut Corp. of America, Union, N. J. He was previously a vice-president of the Mid-Continent Metal Products Co. of Chicago, and during his employment with that Company developed the process and machinery for producing the rollpin fastener. Mr. Peters is a graduate of Purdue University with a B.S. and M.S. in engineering, and was a member of the staff of Battelle Memorial Institute at Columbus. He served in the U. S. Army during the recent war.

Herbert A. Robinson has the job of research metallurgist at Battelle Memorial Institute, Columbus 1, Ohio. He had been with the American Smelting and Refining Co. at Barber, N. J.

Robert Maddin recently accepted the post of assistant professor of mechanical engineering at Johns Hopkins University. He was formerly a research fellow in metallurgy at Yale.

George B. Waterhouse, emeritus professor of metallurgy at MIT, and consulting metallurgist, was awarded an honorary Doctor of Engineering at the recent Nova Scotia Technical College convocation in Halifax. Dr. Waterhouse delivered the convocation address.

Clyde Williams, director of Battelle Memorial Institute, will give the introductory paper on the conservation of iron and steel in production at the United Nations' Scientific Conference on the Conservation and Utilization of Resources on Aug. 25 at Lake Success, N. Y. **John D. Sullivan,** assistant director of Battelle, is scheduled to present a paper on the new processes for the utilization of low-grade ores five days later. The conference is to be scientific rather than policy-making, according to the UN's Economic and Social Council. It will have no power to bind governments and it will not formulate recommendations to them. The practical application of science to resource management and human use will be the primary concern. During the conference papers will be presented by approximately 450 scientists, engineers, and other experts from many countries.

In recognition of significant contributions in the fields of science and public service, the honorary degree of Doctor of Engineering was recently conferred on Mr. Williams by the Michigan College of Mining and Technology. Prior to the presentation, he delivered the commencement address to over 500 candidates of the Michigan graduating class.

Lincoln T. Work

Lincoln T. Work has become associated with Alan R. Lukens at the Powdered Material Research Laboratories, 11 Windsor Street, Cambridge 39, Mass. With the coming of Dr. Work, the organization's field of utility will be widened to undertake work on abrasives, refractories, metal powders, cements, and dusts. He is an authority on grinding, classification, and filtration. Dr. Work had been director of research and development for the Metal and Thermit Corp. for the past nine years. He was on the staff of the chemical engineering department at Columbia University before his affiliation with the Metal and Thermit Corp., and was at that time well known in consulting engineering.

• In Petroleum Circles

Floyd D. Aaring, former University of Oklahoma student, is a petroleum engineer with the Canadian Gulf Oil Co., P. O. Box B-4, Pincher Creek, Alta.

T. H. Acres is on the staff of the Barnsdall Oil Co., Box 367, Newhall, Calif.

George P. Alden, formerly with the U. S. Geological Survey, has the job of petroleum production engineer with the Barnsdall Oil Co., P. O. Box 2039, Tulsa, Okla.

Arnold D. Arnaut graduated in June from the University of Wisconsin's metallurgy department and is employed by Sylvania Electric Products, 35-22 Linden Place, Flushing, L. I., N. Y.

Leo R. Brammer, Jr., who has been studying at the University of Tulsa, is an engineer with the Dempsey Pump Co., Box 3098, Tulsa, Okla.

E. J. Brook is president of the McElroy Ranch Co. of Fort Worth, Texas. He had been with the Franco Wyoming Oil Co.

Robert E. Brooks is working for the Skelly Oil Co. in the Southern division on production. His address for mail is P. O. Box 224, Wynnewood, Okla.

W. T. Cardwell, Jr., formerly with the Standard Oil Co. of California, is senior research engineer for the California Research Corp., La Habra, Calif.

Campbell M. Carothers, district petroleum engineer for the Humble Oil and Refining Co., is addressed at Rt. 1, Raymondville, Texas.

A. L. Carpenter has the post of junior petroleum engineer in the production department of the Humble Oil and Refining Co., Bay City, Texas.

Aaron Cawley, who has been studying at the University of Texas, is now working as engineering trainee for the Honolulu Oil Corp. He can be addressed at Box 1079, Denver City, Texas.

John H. Chain has a job with the American Republics Corp., Box 547, Artesia, N. Mex. He was a student at the University of Texas.

Thomas E. Covington is an engineer trainee with the Tidewater Associated Oil Co., Box 12, Venice, La.

Joseph E. Barthelemy, Jr., who attended the University of St. Louis, is now employed by the Western Geophysical Co., P. O. Box 103, Lac La Biche, Alta.

Rex M. Everett is working for the Magnolia Petroleum Co. in Kermit, Texas. He had been a student at the University of Oklahoma.

Stewart H. Folk has resigned his post at Baylor University in order to accept an assignment with DeGolyer and MacNaughton, consulting geologists and engineers, as their representative in Mexico. His address is now in care of Petroleos Mexicanos, Depto. Exploracion, Rm. 208, Avenida Juarez 95, Mexico City, D. F.

Thomas E. Goebel is in Maracaibo, Venezuela, working for the Cole Drilling Co.

Harold C. Kidd, who attended the University of Tulsa, is on the staff of the Creole Petroleum Corp., Apt. 172, (Laqunillas), Maracaibo, Venezuela.

J. B. Ladd received a B.S. degree in petroleum engineering from the University of Kansas in June and is now employed by The Texas Co. in Cut Bank, Mont.

Kenneth H. Larson, a former student at the Montana School of Mines, is now a junior computer of the Stanolind Oil and Gas Co. His mail address is 1145 Monroe, c/o Stanolind Oil and Gas Co., Seis Party 14, Alexandria, La.

Clinton C. Lieffers, formerly on the staff of the Texas Amerada Petroleum Corp., is now working in the geology department of the Creole Petroleum Corp., Apt. 889, Caracas, Venezuela.

William G. Locke is tar products sales cadet in the tar products division of the Koppers Co., Pittsburgh.

Arthur F. Malicoat is a paleontologist with the Gulf Oil Corp. He receives his mail at his home, 1302 S. 49th St., Temple, Texas.

W. J. Mannas writes that his mail should be addressed to the Pure Oil Co., 35 E. Wacker Drive, Chicago.

William J. McPherson has changed his address from Stanford University to care of Imperial Oil Ltd., 300 9th Ave. W., Calgary, Alta.

Ralph J. Poth has taken a job with the Union Sulphur Co., with Box 511, Sulphur, La., for an address.

Dayton E. Ramsey recently joined the staff of Dowell, Incorporated, Kermit, Texas. He is a former student of Texas A&M.

P. H. Rumsey is addressed in care of the Iraq Petroleum Co., Ltd., (Exploration), Tripoli, the Lebanon. He took the job of junior geologist with the company over a year ago.

H. J. Schroeder has gone to Talara, Peru, as petroleum reservoir engineer with the International Petroleum Co. He had been in the Baroid Sales Division of the National Lead Co. at Houston.

Richard G. Stephens, who studied at the University of Texas at Austin, and was formerly employed by The Texas Co. as a trainee, is at present on active duty in the U. S. Navy. His mail will reach him at 3206 King's Rd., Dallas, Texas.

John F. Stickel, Jr., is a geological engineer with the Wesley, Beford and Stickel Co. of Detroit, Mich.

Todd C. Storer has been transferred by the Stanolind Oil and Gas Co. to Bishop, Texas, where he is field engineer in the Luby area.

Marshall C. Turner is production superintendent for the Continental Consolidated Corp., Long Beach, Calif. He had been with the Union Oil Co.

William E. Topley, a Montana School of Mines student, is now geologist for the Stanolind Oil & Gas Co., 336 8th Ave. West, Calgary, Alta.

Necrology

Date Elected	*Name*	*Date of Death*
1918	Paul Armitage	June 28, 1949
1936	William A. Baueris	Feb. 23, 1949
1936	William Bell	1948
1945	W. A. Bishop	June 10, 1949
1942	T. C. Botterill	June 15, 1949
1947	Tore Flygare	November, 1947
1918	Walter Miller	Unknown
1916	Clarence J. Peterson	May 8, 1948
1904	E. A. Cappelen Smith	June 25, 1949

Proposed for Membership

Total AIME membership on June 30, 1949, was 15,759; in addition 4424 Student Associates were enrolled.

ADMISSIONS COMMITTEE

James L. Head, Chairman; Albert J. Phillips, Vice-Chairman; George B. Corless, T. B. Counselman, Ivan A. Given, George C. Heikes, Richard D. Mollison, and Philip D. Wilson.

Institute members are urged to review this list as soon as the issue is received and immediately to wire the Secretary's office, night message collect, if objection is offered to the admission of any applicant. Details of the objection should follow by air mail. The Institute desires to extend its privileges to every person to whom it can be of service but does not desire to admit persons unless they are qualified.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; AM, Associate Member; S, Student Associate; F. Junior Foreign Affiliate.

ALABAMA

Birmingham — AUSTIN, WILLIAM WYATT, JR. (C/S—J-M). Research metallurgist, Southern Research Institute. SANDELIN, ROBERT WILLIAM. (C/S—J-M). Chief metallurgist, Stockham Values & Fittings, Inc.

ARIZONA

Morenci—BACON, FREDERICK MASON. (AM). Flotation operator, Phelps-Dodge Corp.

Phoenix—POPPINO, CARL ALBERT. (AM). Sales engineer, General Electric Co.

ARKANSAS

Magnolia—ALGER, ROBERT PERDUE. (C/S—J-M). District engineer, Schlumberger Well Surveying Corp.

CALIFORNIA

Alhambra — JAMISON, PAUL HUGUS, JR. (C/S—J-M). Sales promotion engineer, Kobe, Inc. STICK, JOHN C., JR. (C/S—J-M). Chief electrical engineer, Lane-Wells Co.

Bakersfield — CARRICK, HARRY HALL, JR. (C/S—J-M). Resident engineer, General Petroleum Corp. MANGOLD, ROBERT P. (C/S—J-M). Petroleum engineer, Independent Exploration Co. PERRY, CLYDE WILBERT. (C/S—J-M). Division petroleum engineer, Richfield Oil Corp. YAMAMOTO, ROY HIDEO. (R,C/S—S-J). Assistant engineer, bottom-hole lab., Core Laboratories, Inc.

Berkeley—PARKER, EARL R. (C/S—J-AM). Associate professor of metallurgy, University of California. WICKETT, WALTON AMES. (R,C/S—S-M). Western sales manager, Tracerlab, Inc.

Huntington Park — ANDERSON, JAMES LOUIS. (M). Chief engineer, Conveyor Co. WISEMAN, KENNETH WILLIAM. (J). Trainee-petroleum engineering, Socony-Vacuum Oil Co.

La Habra — SWENY, JOHN WILLIAM. (C/S—J-M). Associate research engineer, California Research Corp.

Lompoc — GRIMM, KENNETH E. (C/S—J-M). Paleontologist, Johns-Manville Products Corp.

Long Beach — CARRIEL, JAMES TURNER. (C/S—J-M). Petroleum engineer, Southwest Exploration Co. HILTY, GEORGE CLIFFORD. (C/S—J-M). Petroleum engineer, Long Beach Harbor Dept. INSKEEP, WILLIAM DOLMAN. (M). Drilling contractor.

Los Angeles — BEAL, CARLTON. (C/S—J-AM). Consulting petroleum engineer. LESTER, GRAHAM WALLACE. (J). Engineer's assistant, Union Oil Co. of California. MASON, HAMILTON. (C/S—J-M). Service engineer, North American Aviation, Inc.

Orcutt—HILTON, ALFRED GEORGE. (M). Division drilling foreman, Union Oil Co. of California.

Pasadena—OLSEN, HAROLD TORMOD. (C/S—J-M). Petroleum engineer, Superior Oil Co. TAYLOR, JACK LESLIE. (C/S—J-M). Research engineer, jet propulsion lab., California Institute of Technology. TROMBLE, JAMES PREMONT. (C/S—J-M). Engineer inspector, Bureau of Power and Light.

Sacramento — LANG, HENRY ADOLPH. (C/S—J-M). Sales engineer, Ingersoll-Rand Co.

San Francisco — RUHLMAN, FRED LEE. (C/S—J-AM). Commander, U. S. Navy. WOOD, GERRIT V. (AM). Western sales manager, Taylor-Wharton Iron and Steel Co.

San Marino—WOODWARD, ALBERT FLETCHER. (C/S—J-AM). Senior petroleum engineer, Union Oil Co.

Whittier — FRASER, JOHN REID. (C/S—J-M). Division engineer, Union Oil Co. of California. ZINSZER, RICHARD HOWARD. (C/S—J-M). Group leader-research, Union Oil Co.

COLORADO

Climax—HARTMAN, LOUIS WOODSON. (J). Resident geologist, Climax Molybdenum Co. KMINEK, JOHN MILAN. (C/S—S-J). Engineer, Climax Molybdenum Co.

Denver—BARNES, JOHN WALLACE (C/S—J-M). Engineer, mining dept., Stearns-Roger Mfg. Co. MATTSON, TAUNO OTTO HENRY. (C/S—J-M). Division petroleum engineer, The Texas Co.

Gilman—VITZ, HOWARD ENGELER (C/S—J-M). Geologist, New Jersey Zinc Co.

Pueblo — ZADRA, JOHN ROBERT. (C/S—J-M). Assistant chief metallurgist, Colorado Fuel and Iron Corp.

CONNECTICUT

Cheshire — BURRALL, STEPHEN HART. (M). Representative, central technical dept., American Brass Co.

S. Norwalk — MANNING, JOHN PEARCE, JR. (C/S—J-AM). Draftsman designer, Anaconda Copper Mining Co.

Waterbury—KIRBY, PHILIP HULL. (R,C/S—J-M). Metallurgical engineer, American Brass Co.

Watertown — CANDEE, ELLSWORTH T. (C/S-J-AM). Director of research and development, Lea Mfg. Co.

DISTRICT OF COLUMBIA

Washington—LINDBERG, RUSSELL AXEL. (C/S—J-M). Metallurgist, National Bureau of Standards.

FLORIDA

Jacksonville—BROWN, D. GRANT.

(M). Vice-president, Humphreys Gold Corp.

IDAHO

Kellogg — REYNOLDS, JOHN R. (C/S—J-M). Partner, Preston & Reynolds.

Moscow — PRATER, LEWIS SEWARD. (C/S—J-M). Assistant director, Idaho Bureau of Mines and Geology.

Patterson — McFARLANE, JAMES CARL. (C/S—J-M). Chief engineer, Bradley Mining Co.

ILLINOIS

Centralia — CAMERON, CHARLES VINCENT. (C/S—J-M). Division exploitation engineer, Shell Oil Co.

Chicago — HESS, JAMES BROWN. (C/S—J-M). Metallurgist, Institute for Study of Metals, University of Chicago. JUSTER, NATHAN B. (C/S—J-M). Metallurgist, Inland Steel Co. MARTIN, PASCHAL. (C/S—J-M). Chief production engineer, Pure Oil Co. ZENER, CLARENCE. (C/S—J-M). Professor of physics, University of Chicago.

Cicero—KIZIOR, JEROME JOSEPH. (C/S—S-J).

Danville—OBRIG, VICTOR J. (C/S—J-M). Metallurgical engineer, central foundry div., General Motors.

Flora—BROWN, BOB DIGGS. (M). Division engineer, Halliburton Oil Well Cementing Co.

Peoria—LEBER, SAM. (C/S—S-J).

Salem — WRIGHT, FRED S., JR. (C/S—J-M). District petroleum engineer, Magnolia Petroleum Co.

Urbana — SEITZ, FREDERICK. (C/S—J-AM). Research professor, University of Illinois.

Winnetka — BURGOYNE, WILLIAM RICHARD. (C/S—J-M). Production manager, U. S. Gypsum Co.

INDIANA

East Chicago—SQUARCY, CHARLES M. (C/S—J-M). General foreman, Inland Steel Co.

Hammond—DANCHI, GEORGE. (J). Student, Purdue University.

Terre Haute—TOELLE, HARRY A., JR. (C/S—S-J). Junior mine shift boss, Braden Copper Co.

LOUISIANA

Bernice — TAYLOR, CLARENCE PIERCE. (J). Junior petroleum engineer, Hunt Oil Co.

New Orleans — LANGHETEE, EDMOND JOSEPH, JR., (J). Junior engineer, Louisiana Land and Exploration.

Shreveport—MELTZER, LEE HILLIARD. (C/S—J-M). Geologist, Union Producing Co.

MARYLAND

Baltimore — McGAVOCK, CECIL BILLUPS, JR. (C/S—J-M). District geologist, Corps of Engineers, Baltimore District, U. S. Army.

Silver Spring—ST. CLAIR, HILLARY W. (C/S—J-M). Metallurgist-in-charge, Metals Recovery & Refining Section, Bureau of Mines.

MASSACHUSETTS

Attleboro — PETERSON, ARTHUR WILLIAM (C/S—J-M). Metallurgical engineer, assistant professor, MIT.

Cambridge — BAIRD, WALTER SCOTT. (C/S—J-AM). President, Baird Associates, Inc.

Reading — DASHER, JOHN ORNDOFF. (C/S—J-M). Executive officer mineral engineering lab., MIT.

MICHIGAN

Bay City — SIMONS, JEROME. (J).

Bessemer—EASTMAN, EUGENE ALBERT. (C/S—S-J). Student, Michigan College of Mining & Technology.

Coldwater—GRAY, LATHAM BURBERRY, JR. (C/S—S-J).

Detroit—SCHWARTZ, DONALD L. (C/S—J-M). Research metallurgist, Carboloy Co.

Gwinn — MARIN, MARTIN JOHN. (C/S—S-J).

Ironwood — CHRISTENSON, ALFRED JOHN, JR. (C/S—S-J).

Ishpeming — PETERSON, BERNHARDT HERBERT. (J). Production engineer, Cleveland-Cliffs Iron Co.

MINNESOTA

Ely—BERKNER, DONALD A. (C/S—J-M). Mining engineer, Pioneer mine, Oliver Iron Mining Co.

MISSISSIPPI

Jackson—WEBB, SAM NAIL. (C/S—J-M). Assistant division geologist, Honolulu Oil Corp.

MISSOURI

Rolla — FINE, MORRIS MILTON. (C/S—J-M). Senior metallurgist, Metallurgical Branch, Bureau of Mines.

MONTANA

Butte — WAYLETT, WILLIAM JAMES. (C/S—J-M). Assistant mine engineer, Mining Engineering Dept., Anaconda Copper Mining Co.

NEVADA

Pioche—DURK, ROBERT ROY. (M). Assistant superintendent, Combined Metals Reduction Co.

NEW JERSEY

Hackettstown—FEDUSKA, STEPHEN LESTER. (C/S—J-M). Foundry superintendent, Thomas & Skinner Co.

Kearny—SMITH, GEORGE V. (C/S—J-M). Research metallurgist, research lab., U. S. Steel Corp.

Orange—PREUSCH, CHARLES DANIEL. (C/S—J-M). Metallurgist, Crucible Steel Co., of America.

Summit—MARBLE, EARL ROBERT, JR. (C/S—J-M). Metallurgical engineer, American Smelting & Refining Co.

NEW MEXICO

Albuquerque — ITALIA, SANTO (C/S—S-AM). Student, Classified training, USAF.

NEW YORK

Glen Cove — McGAULEY, PATRICK JOHN. (C/S—J-M). Project engineer, Chemical Construction Corp.

Jackson Heights — LANDA, MAYNARD IVAN. (M). Manager, economics and statistics, Petroleum Advisers, Inc.

Kenmore—BRAY, JOSEPH MOYER. (C/S—J-M). Director of mining division, Osmose Wood Preserving Co.

Lewiston — OFFENHAUER, CHARLES MARTIN. (C/S—J-M). Research metallurgist, Union Carbide & Carbon Research Labs.

New York — CHANG, LO CHING. (C/S—J-M). Research metallurgist, Crucible Steel Co. of America. LANGE, ESWORTHY PAUL. (C/S—J-M). Operating manager, Saudi Arabian Government Gypsum Project. ROBERTS, BEN DAVID. (C/S—J-M). Ore buyer, American Smelting & Refining Co. ULRICH, GEORGE H., JR. (AM). District engineer, Link Belt Co.

Ozone Park — SCHNITZEL, RANDOLPH HUFF. (J).

Rye—BIER, CECIL JOSHUA. (C/S—J-M). Chief engineer, Powmetco, Inc.

Saratoga Springs—CLUGSTON, EDGAR JOSEPH. (M). Division head, metallurgical processing division, Saratoga Labs., Inc.

Schenectady—COFFIN, LOUIS FUSSELL, JR. (M). (After Sept., 1949), Research associate, General Electric Co. HARRINGTON, RICHARDS HARRY. (M). Research associate, General Electric Co.

Tahawus—MEAD, JOSEPH CHARLES. (R,C/S—S-M). Sinter plant superintendent, National Lead Co.

Tonawanda — McCANDLESS, EDWARD L. (C/S—J-M). Assistant superintendent, research lab., Linde Air Products Co.

Tuckahoe — MOLLISON, RICHARD D. (C/S—J-M). Mining engineer, Texas Gulf Sulphur Co.

Yonkers—MARTIN, WILLIAM DAY. (C/S—J-M). Production engineer, Tide Water Associated Oil Co.

OHIO

Cincinnati—BARTON, FRANK PRESTON. (C/S—J-M). Cincinnati branch manager, metallic products div., Eagle-Picher Co.

Cleveland — CAREY, ROBERT S. (AM). Iron ore sales, Pickands Mather & Co. HUNSICKER, HAROLD YUNDT. (C/S—J-M). Assistant chief, Cleveland research div., Aluminum Research Labs., Aluminum Co. of America. STEFAN, PETER. (C/S—J-M). Development engineer, Alloy Metal Wire Co.

Cleveland Heights—HRUBY, THOMAS F. (C/S—S-J).

Columbus — BECKER, THEODORE W. (C/S—S-J). CHASE, THOMAS LOUIS. (C/S—S-J). Metallurgist, Williams & Co., Inc. ELSEA, ARTHUR RAY. (C/S—J-M). Assistant supervisor, Battelle Memorial Institute. GREENIDGE, CHARLES TURNER. (C/S—J-M). Research supervisor, Battelle Memorial Institute. MEADERS, ROBERT C. (C/S—J-M). Research engineer, Battelle Memorial Institute. PILCHER, JOHN MASON. (C/S—J-M). Research engineer, fuels div., Battelle Memorial Institute. SMITH, EUGENE MONROE. (C/S—J-M). Research engineer, Battelle Memorial Institute. SPRETNAK, JOSEPH WILLIAM. (C/S—J-M). Associate professor of metallurgy, Ohio State University.

Columbus Grove—BASINGER, VIRGIL D. (C/S—S-AM). Metallurgical engineer, Cincinnati Milling Machine Co.

Elyria — HOEL, ALFRED G., JR. (C/S—J-M). Vice-president, Concrete Masonry Corp.

Findlay — DUMBROS, NICHOLAS GEORGE. (C/S—J-M). Economist, Ohio Oil Co.

Newark — CARTER, ANTHONY J., JR. (R,C/S—S-J). Division production engineer, Pure Oil Co.

Portsmouth — LENHART, ROBERT EUGENE. (C/S—S-J). Member, Scientific Training Program, General Electric Co.

Powell — LYONS, ORVILLE RICHARD. (C/S—J-M). Research engineer in charge of coal preparation, Battelle Memorial Institute.

OKLAHOMA

Bartlesville — DEAN, MAURICE R. (M). Senior chemical engineer, Phillips Petroleum Co. PRANGE, FREDERICK A. (C/S—J-M). Metallurgical engineer, Phillips Petroleum Co.

Healdton — STITT, IRA BEY, JR. (C/S—J-AM). District engineer, Magnolia Petroleum Co.

Oklahoma City — WASZOWSKI, HENRY LOUIS, JR. (C/S—J-M). Division petroleum engineer, Magnolia Petroleum Co.

Ponca City — REYNOLDS, JACK J. (C/S—J-M). Supervising research engineer, Continental Oil Co.

Tulsa — BARTON, ROBERT CLINTON. (R,C/S—S-AM). Production engineer, Gulf Oil Corp. CARUTHERS, C. B. (C/S—J-M). Unitization superintendent, Stanolind Oil & Gas Co. CHAPELL, DONALD OWEN. (M). Vice-president, exploration and land dept., Sunray Oil Corp. CONNER, JAMES CLARK. (C/S—J-M). Contract sales engineer, Stanolind Oil & Gas Co. FRANCIS, ALEX WALLACE, JR. (C/S—J-M). Assistant chief engineer, National Tank Co. STEARNS, GLENN M. (C/S—J-M). Development superintendent, Stanolind Oil & Gas Co.

OREGON

Portland—HATTAN, ELTON MUMPOWER. (M). Field examiner (mining), Bureau of Land Management, Department of the Interior. MASON, RALPH S. (C/S—J-M). Mining engineer, Oregon Dept. of Geology and Mineral Industries.

PENNSYLVANIA

Bethlehem — EBERHARDT, JOHN ERNST. (C/S—J-M). Engineer, Bethlehem Steel Co.

Cornwall — OLSEN, HAROLD OLIVER. (C/S—J-M). Superintendent, Bethlehem Steel Co.

Edgewood—BANK, WALTER. (C/S—J-M). Chemist-petrographer, Bureau of Mines.

Forty Fort — ARBOGAST, KARL FRANK. (M). General manager, Lehigh Valley Coal Co.

Glenshaw — GROW, GEORGE COPERNICUS, JR. (C/S—J-M). Geologist, People's Natural Gas Go.

Johnstown—STOTZ, EDWARD WESLEY, (C/S—S-J). Metallurgist, Bethlehem Steel Co.

Kingston—MORGAN, DANIEL JOHN. (AM). Sales engineer, Hazard Insulated Wire Works. WEICHEL, THOMAS ROBERT. (M). Mining-electrical engineer, Hazard Insulated Wire Works.

Masontown — GIROD, MICHAEL B. (M). Mine superintendent, H. C. Frick Coke Co.

Northampton — ANTHONY, STANLEY EDWARD. (M). Flotation engineer, Separation Process Co.

Philadelphia — JAMIESON, ARCHIBALD LIVINGSTON. (C/S—J-M). Metallurgist, Frankford Arsenal.

Pittsburgh—BRANCH, RAE WELLS. (AM). Manager, Pittsburgh district office, Whitney Chain & Mfg. Co. HAWKES, MALCOLM FRANK. (C/S—J-M). Associate professor of metallurgical engineering, and member of staff, metals research lab., Carnegie Institute of Technology. LIPANOVICH, AUGUST JOHN. (C/S—J-M). Assistant ceramist, Vesuvius Crucible Co. SERGY, WALTER THOMAS. (J). Steel works metallurgist, Pittsburgh works, Jones & Laughlin Steel Corp.

Wilkes-Barre—KOPPELMAN, JACK KEITH. (C/S—S-J). Sales engineer, Goodman Mfg. Co. STOTT, ROY GEORGE. (C/S—J-M). Mining engineer, Bureau of Mines.

Wyoming—WEIR, JOSEPH STANLEY. (M). Civil engineer, Bureau of Mines.

SOUTH DAKOTA

Lead—KELLAR, KENNETH CHAMBERS. (R—AM). Assistant chief counsel, Homestake Mining Co.

TENNESSEE

Columbia—AALL, CHRISTIAN HIORTH. (AM). Research field technologist, Monsanto Chemical Co.

Knoxville—LAURENCE, ROBERT A. (C/S—J-M). Regional geologist, U. S. Geological Survey.

TEXAS

Abilene—JENKE, ARTHUR L. (C/S—J-M). Engineer in charge of lab., Abilene Sample Log Service and Core Labs.

Austin—HALL, JAMES AUGUSTUS, JR. (C/S—J-M). Senior petroleum engineer, R. R. Commission of Texas. LEBEAUX, JACOB M. (J). Assistant professor of petroleum engineering, Univ. of Texas.

Bay City—CARPENTER, ALBERT LEWIS. (C/S—S-AM). Jr. petroleum engineer, Humble Oil & Refining Co.

Corpus Christi—WATERMAN, CHARLES NATHAN. (M). Plant manager, American Smelting & Refining Co.

Dallas—COLDWELL, CHARLES HATTON. (C/S—J-M). Exploitation geologist, Sun Oil Co. DAVIS, LOUIS FREEMAN. (C/S—J-M). Senior mechanical engineer, Atlantic Refining Co. KEATING, J. PATRICK. (C/S—S-J). Petroleum engineer, Magnolia Petroleum Co. MYERS, RICHARD. (C/S—J-M). Petroleum engineer, Magnolia Petroleum Co. PATTON, E. CHARLES, JR. (C/S—J-M). In charge of reservoir engineering, Magnolia Petroleum Co. TAYLOR, EARLE FREDERICK. (C/S—J-M). Geologist, DeGolyer & MacNaughton.

Fort Worth—GEROLDE, STEVEN. (C/S—J-M). District petroleum engineer, Gulf Oil Corp. WILEY, PAUL M. (C/S—J-M). Division reservoir engineer, The Texas Co.

Freer—BARRETT, WARREN JEFFERSON. (M). Assistant district superintendent, Humble Oil & Refining Co.

Ganado—ELLIS, JOHN EDWIN. (J). Field engineer, The Texas Co.

Graham—WILLIBRAND, ALPHONSE FRED. (M). District manager, Schlumberger Well Surveying Corp.

Houston—BLACK, IRA LESTER. (J). Portable laboratory supervisor (Houston area), Shell Oil Co. BORN. HOWARD R. (C/S—J-M). Reserve geologist, Tennessee Gas Transmission Co. CALHOUN, GEORGE HENRY. (M). Division mechanical engineer, Shell Oil Co. CRANDALL, JOHN RODERIC. (C/S—J-M). Petroleum engineer, Humble Oil & Refining Co. RAGLAND, DOUGLAS. (C/S—J-M). Assistant chief petroleum engineer, Humble Oil & Refining Co. RASSINIER, EDGAR A. (C/S—J-M). Senior engineer, Phillips Petroleum Co. YALE, WILLIAM DICKINSON. (C/S—J-M). Chief engineer, gas division, The Texas Co.

Kermit—MILLICAN, MARCUS LAVERNE. (J). District engineer, Schlumberger Well Surveying Corp.

Kilgore—BUTTS, JAMES ALVIS, JR. (C/S—J-M). District engineer, Tide Water Associated Oil Co.

Livingston—FAIN, CLEMENT FRANKLIN, III. (C/S—S-J). Trainee, The Texas Co.

Lubbock—COWART, DAVID M. (J). Engineer in charge of location, Schlumberger Well Surveying Corp.

Madisonville—ELLSWORTH, RALPH IRVING. (J). Junior petroleum engineer, American Republics Corp.

Midland—CURTIS, THOMAS M. (C/S—J-M). District engineer, Stanolind Oil & Gas Co. PERUSEK, CYRIL J. (C/S—J-M). Geologist, Residue Research Lab. SPEERS, FRED HENRY. (C/S—J-M). Petroleum engineer, The Superior Oil Co.

Odessa—CALDER, NORMAN BRUCE. (C/S—S-J). Petroleum engineer, Gulf Oil Corp. HOCKADAY, DONALD EMMETT, JR. (J). Engineer, Kewanee Oil Co. RABE, CHARLES LEONARD. (C/S—J-M). Division exploitation engineer, Shell Oil Co.

Premont—FRANKLIN, LEONARD ODELL. (C/S—S-J). Petroleum engineer, Magnolia Petroleum Co.

Wichita Falls—PARKER, ROBERT GRAY. (C/S—J-M). Assistant district superintendent, Wichita Falls District, Continental Oil Co.

UTAH

Lark—McCONNELL, WALTER FREDRICK. (AM). Mucker, U. S. Smelting Refining & Mining Co.

Magna—RIBOTTO, JOE W. (C/S—J-M). General mill foreman, Utah copper div., Kennecott Copper Corp.

Salt Lake City—apROBERTS GWILYM EVAN. (M). Sales engineer, Cate Equipment Co. SPRAGUE, RODNEY BRYANT. (C/S—J-M). Geologist, American Smelting & Refining Co. SUMSION, HENRY THEODORE (C/S—J-M). Research assistant, Univ. of Utah.

VIRGINIA

Arlington—McMAHON, ALBERT DANIEL. (R,C/S—S-M). Industrial engineer, Munitions Board.

Radford—MARTIN, CLOYD. (M). General manager and superintendent, Great Valley Anthracite Coal Corp.

WASHINGTON

Opportunity—LOWRY, JOHN WILLIAM. (C/S—S-J). Process metallurgist, division of metallurgical research, Permanente Metals Corp.

Tacoma—ANDERSON, KENNETH H. (C/S—J-M). Assistant superintendent, American Smelting & Refining Co.

Wenatchee—HOFF, FRED JAMES. (C/S—J-M). Manager, Central Tractor & Equipment Co.

WISCONSIN

Clintonville—BERKHAHN, ROBERT WILLIAM. (C/S—S-J). Metallurgist, American Smelting & Refining Co.

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WYOMING

Casper—BARNETT, JOSEPH H. (C/S—J-M). Division engineer, Stanolind Oil & Gas Co. FALKINGHAM, DONALD HERBERT. (R,C/S—S-M). Petroleum engineer, Stanolind Oil & Gas Co.

ALASKA

Anchorage—NAPPE, LESLIE ERVING. (R,C/S—S-M). Sales engineer, Yukon Equipment, Inc.

BRITISH COLUMBIA

Tulsequah—ROBINSON, GEORGE WILLARD. (C/S—J-M). Mine manager, Polaris-Taku Mining Co.

NORTHWEST TERRITORY

Yellowknife—GROGAN, KENNETH CRAWFORD. (C/S—J-M). Mill superintendent, Giant Yellowknife Gold Mines, Ltd.

ONTARIO

Haileybury—KEEFER, THOMAS COLTRIN. (C/S—J-M). Field engineer, Mines Operating Co.

Ottawa—CONVEY, JOHN (M). Chief metallurgist, Bureau of Mines, Ottawa.

Port Arthur—BARTLEY, MELVILLE WILLIAM. (C/S—J-M). Principal, Lakehead College & Technical Institute.

Schumacher—SMITH, JOHN. (J). Research foreman, production engineering dept., Hollinger Consolidated Gold Mines, Ltd.

SAN LUIS POTOSI

Wadley—ARCHIBALD, JOHN CHRISTIE, JR. (C/S—J-M). General superintendent, Cia. Minera y Refinadora Mexicana.

SINALOA

Mazatlan—CONTRINI, ATTILIO S. (R—M). Superintendent, Metalurgica Occidental S. A.

SONORA

Cananea—LOVING, JOHN CLYDE. (C/S—J-M). Mill metallurgist, Cananea Consolidated Copper Co.

BRAZIL

Minas Gerais—FRANK, VIRGIL EVERETT. (C/S—J-M). Assistant mine superintendent, Cia. Vale do Rio Doce.

Sao Paulo—MORAES, ANTONIO ERMIRIO. (J). Engineer, S. A. Industrias Votorantin. MORAES, JOSE E., JR. (C/S—S-J). Engineer, S. A. Industrias Votorantin.

CHILE

Potrerillos—SOBRAL, DANIEL MARTINEZ. (C/S—J-M). Section mine foreman, Andes Copper Mining Co.

PERU

Oroya—BLACK, ANDREW BAXTER. (C/S—J-M). Anode residue plant foreman, Cerro de Pasco Copper Co.

VENEZUELA

Bolivar—WITTMEYER, WILLIAM WOOLSEY. (C/S—S-J). Mine foreman, Guayana Mines, Ltd.

Caracas—ROOKUS, JAMES DUDLEY. (C/S—J-M). Party chief, United Geophysical Co. WIDNER, GEORGE WASHBURN. (J). Petroleum engineer, Creole Petroleum Corp. WISE, M. SMITH, JR. (C/S—J-M). District petroleum engineer, Texas Petroleum Co.

GERMANY

Landgraf Philippotr—GOTTE, AUGUST. (R—M). Works leader, Deutsche Gold & Silver Schneidenstalt.

PORTUGAL

Lisbon—SALEMA GARCAO, JOSE CAETANO. (M). Mine operator, Baralt Tin & Wolfram Co.

SWEDEN

Munkfors—MOLINDER, ANDERS GORAN. (C/S—S-J). Metallurgist, Uddeholm Co., Munkfors Bruk.

UNION OF SOUTH AFRICA

Kimberley—GALLAGHER, WILLIAM STANLEY. (M). Assistant general manager, De Beers Consolidated Mines.

INDIA

Calcutta—AZIM, SYED ANWARUL. (C/S—S-J). Sales supervisor, Caltex (India), Ltd.

JAPAN

Tokyo—HASIGUTI, RYUKITI. (M). Assistant professor of physical metallurgy, Univ. of Tokyo.

NEW SOUTH WALES

Cobar—MORGAN, JOHN PHILIP. (C/S—J-M). Underground superintendent, New Occidental Gold Mines.

Lithgow—WOODWARD, HARRY BERTRAM. (M). Sales representative, Joy Sullivan Machinery Co.

NEW ZEALAND

Dunedin—FITZWILLIAM, JOHN BRUCE HOPE. (C/S—S-J). (Commencing Sept. 1, 1949), Research fellow in mining engineering, Missouri School of Mines & Metallurgy.

STUDENT ASSOCIATES

Elected July 27, 1949

Kevin M. Barry	St. Louis Univ.
Warren A. Brown, Jr.	Univ. Okla.
Gerald A. Cleary	Mich. Min. & Tech.
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Equilibrium in the Reaction of Hydrogen with Oxygen in Liquid Iron

MINU N. DASTUR,* Student Associate, and JOHN CHIPMAN,† Member AIME

The importance of dissolved oxygen as a principal reagent in the refining of liquid steel and the necessity for its removal in the finishing of many grades have stimulated numerous studies of its chemical behavior in the steel bath. From the thermodynamic viewpoint the essential data are those which determine the free energy of oxygen in solution as a function of temperature and composition of the molten metal. A number of experimental studies have been reported in recent years from which the free energy of oxygen in iron-oxygen melts can be obtained with a fair degree of accuracy for temperatures not too far from the melting point. Certain discrepancies remain, however, which imply considerable uncertainty at higher temperatures; also several sources of error were recognized in the earlier studies. It has been the object of the experimental work reported in this paper to reexamine these sources of uncertainty and to redetermine the equilibrium condition in the reaction of hydrogen with oxygen dissolved in liquid iron.

The reaction and its equilibrium constant are:

$$H_2\,(g) + \underline{O} = H_2O\,(g);\qquad K_1 = \frac{p_{H_2O}}{p_{H_2} \times \%\,O} \qquad [1]$$

Here the underlined symbol $\underline{O}$ designates oxygen dissolved in liquid iron. The activity of this dissolved oxygen is known to be directly proportional to its concentration[1,2] and is taken as equal to its weight percent.

The closely related reaction of dissolved oxygen with carbon monoxide has also been investigated:[3,4,5]

$$CO\,(g) + \underline{O} = CO_2\,(g);\qquad K_2 = \frac{p_{CO_2}}{p_{CO} \times \%\,O} \qquad [2]$$

The two reactions are related through the water-gas equilibrium:

$$H_2\,(g) + CO_2\,(g) = CO\,(g) + H_2O\,(g);\qquad K_2 = \frac{p_{CO} \times p_{H_2O}}{p_{H_2} \times p_{CO_2}} \qquad [3]$$

and with the aid of the accurately known equilibrium constant of this reaction, it has been shown[5] that the experimental data on reactions [1] and [2] are in fairly good, though not exact, agreement.

Experimental Method

Great care was taken to avoid the principal sources of error of previous studies, namely, gaseous thermal diffusion and temperature measurement. The apparatus was designed to provide controlled preheating of the inlet gases and to permit the addition of an inert gas (argon) in controlled amounts, two measures found to be essential for elimination of thermal diffusion. A known mixture of water vapor and hydrogen was obtained by saturating purified hydrogen with water vapor at controlled temperature. This mixture, with the addition of purified argon, was passed over the surface of a small melt (approximately 70 g) of electrolytic iron in a closed induction furnace. After sufficient time at constant temperature for attainment of equilibrium the melt was cooled and analyzed for oxygen.

GAS SYSTEM

A schematic diagram of the apparatus is shown in Fig 1. Commercial hydrogen is led through the safety trap *T* and the flowmeter *F*. The catalytic chamber *C*, held at 450°C, was used to convert any oxygen into water-vapor. A by-pass *B* with stopcocks was provided so that the hydrogen could be introduced directly from the tank to the furnace when desired. From the catalytic chamber the gas passed through a water bath *W*, kept at the desired temperature by an auxiliary heating unit, so that the gas was burdened with approximately the proper amount of water vapor before it was introduced into the saturator *S*.

All connections beyond the catalytic chamber were of all-glass construction. Those connections beyond the water bath were heated to above 80°C to prevent the condensation of water vapor. After the saturator, purified argon was led into the steam-hydrogen line at *J*, and finally the ternary mixture was introduced into the furnace.

THE SATURATOR

The saturator unit comprised three glass chambers, as shown in Fig 1, the first two chambers packed with glass beads and partially filled with water, and the third empty. Each tower had a glass tube with a stopper attached for the purpose of adjusting the amount of water in it. The unit was immersed in a large oil bath, which was automatically controlled with the help of a thermostat relay to constant temperature, ±0.05°C, using thermometers which had been calibrated against a standard platinum resistance thermometer. The performance of the saturator over the range of experimental conditions was checked by weighing the water absorbed from a measured volume of hydrogen; the observed ratio was always within 0.5 pct of theoretical.

New York Meeting, February 1950.
TP 2661 C. Discussion of this paper (2 copies) may be sent to *Transactions* AIME before April 1, 1950. Manuscript received March 31, 1949.
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* Metallurgical Engineer, H. A. Brassert & Co., New York.

† Professor of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

[1] References are at the end of the paper.

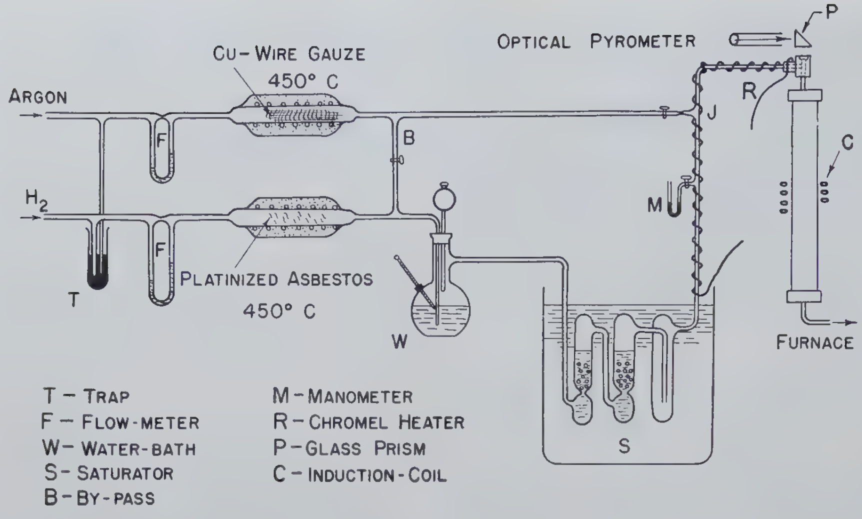

FIG 1—Diagram of apparatus.

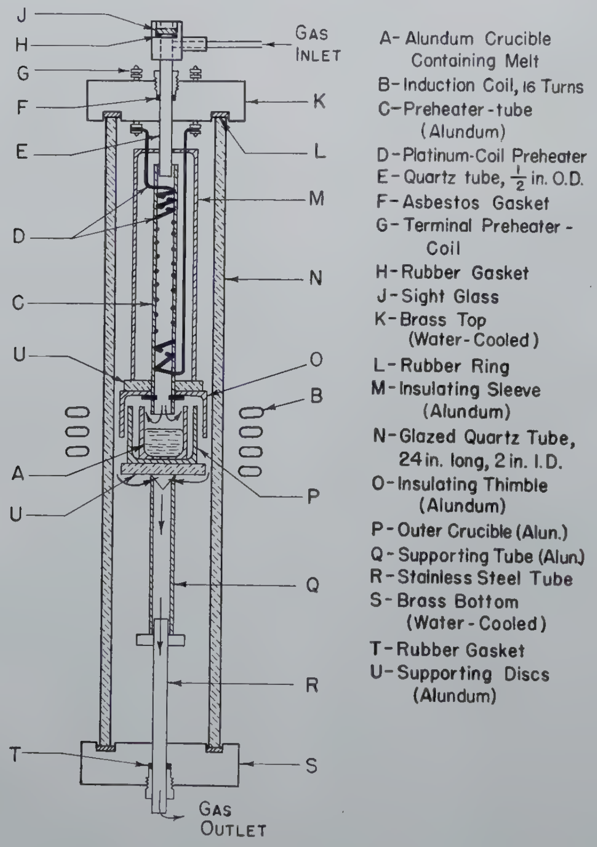
J
H
G
F
E
D
C
U
A
U
T
Gas Inlet
K
L
M
N
O
B
P
Q
R
S
Gas Outlet
A - Alundum Crucible Containing Melt
B - Induction Coil, 16 Turns
C - Preheater-tube (Alundum)
D - Platinum-Coil Preheater
E - Quartz tube, 1/2 in. O.D.
F - Asbestos Gasket
G - Terminal Preheater-Coil
H - Rubber Gasket
J - Sight Glass
K - Brass Top (Water-Cooled)
L - Rubber Ring
M - Insulating Sleeve (Alundum)
N - Glazed Quartz Tube, 24 in. long, 2 in. I.D.
O - Insulating Thimble (Alundum)
P - Outer Crucible (Alun.)
Q - Supporting Tube (Alun)
R - Stainless Steel Tube
S - Brass Bottom (Water-Cooled)
T - Rubber Gasket
U - Supporting Discs (Alundum)

FIG 2—Furnace arrangement.

FURNACE ARRANGEMENT

The furnace arrangement is shown in Fig 2. A glazed-surface silica tube *N*, 24 in. long and 2 in. id, was used throughout. It worked satisfactorily and was impermeable to gases at elevated temperatures. The furnace was equipped with water-cooled brass top *K* and bottom *S* and rubber gaskets *L*. The brass head *K* was fitted with a sight glass *J* made of pyrex glass, ½ in. diam and 1/16 in. thick. A gas inlet and outlet were provided at the top and bottom of the furnace respectively. A small silica tube, ½ in. od and 5 in. long, was used to carry the mixture into the furnace. It was fixed to the furnace head by means of an asbestos gasket *F*. The preheater tube *C* was suspended from the small silica tube.

The alumina crucible *A* was placed inside an outer alundum thimble *P*, resting on an alundum disc *U* which was in turn supported on top of an alundum tube *Q*, ½ in. id, and steel tube *R* which passed through the bottom by means of a rubber gasket and which could be slid up or down as desired. This proved to be very effective in positioning the melt inside the induction coil *B* to get the desired electrical coupling. The power needed for melting was from 10 to 14 kw, supplied by a 35 kva high frequency unit, and only 5 to 8 kw were necessary to hold the metal at any temperature between 1535° and 1800°C.

THE PREHEATER

The preheater tube *C* made of alundum, ½ in. id, was tapped with 12 threads to the inch for a length of 6 in.; a coil of platinum wire *D*, 0.025 in. diam, which served as the heating element, was screwed into position in the threads. Later on, a bigger and better preheater was made 9 in. long and with a heavier wire, 0.030 in. diam, using platinum-10 pct rhodium instead of pure platinum. This enabled the entering gaseous mixture to be heated up to the temperature of the melt before coming in contact with it. The leads were taken out through holes drilled in the preheater tube and were fastened to terminal connectors at *G*. The preheater was covered with an alundum insulating sleeve *M*, 12 in. long and 1½ in. diam, resting on an alundum disc *U* and another sleeve *O*, 1½ in. long and 1¾ in. diam, to prevent excessive radiation. The incoming gases came in direct contact with the heated platinum wire and hence the preheating was very efficient.

OXYGEN ANALYSIS

Oxygen analyses were made by the vacuum fusion method on an apparatus which has been used in this laboratory for over ten years. It had been calibrated previously against measured gas volumes and checked by exchange of samples with the National Bureau of Standards. Results reported are the mean of two or more concordant determinations.

AVOIDANCE OF THERMAL DIFFUSION

In a mixture of gases of unlike molecular weight any temperature gradient tends to produce corresponding composition gradient, the lighter gas diffusing toward the hotter region. This is a well known effect which has given rise to troublesome errors in many studies of gas-metal reactions. When the metal is heated by induction a sharp temperature gradient may be set up near its surface; in some of the early

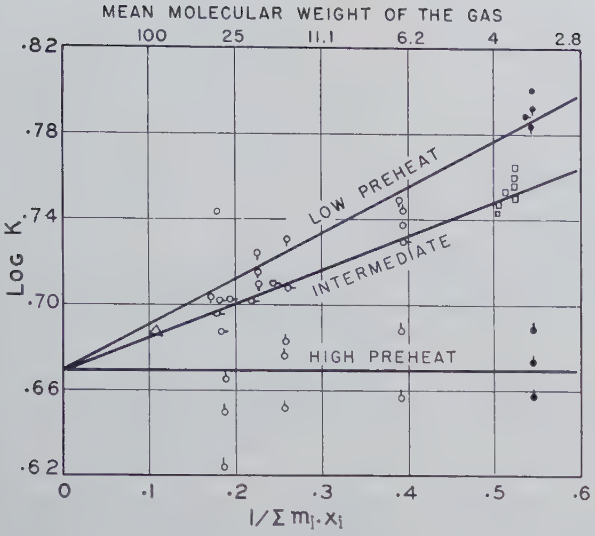

FIG 3—Experimental values of the apparent equilibrium constant at 1563° C. Log *K* approaches a limiting true value with addition of inert gas of high molecular weight.

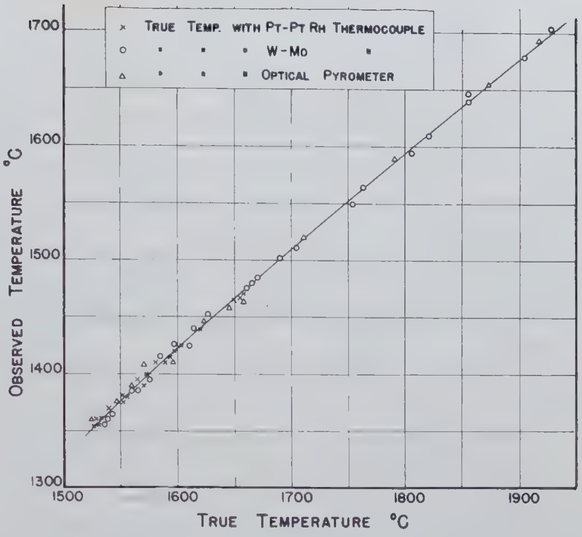

FIG 4—Calibration curve for optical pyrometer sighted on a clean surface of liquid iron.

studies of reaction [1] this resulted in apparent values of K_1 which are now known to have been too high.

A study of the factors affecting thermal diffusion[6] indicated two practical methods of minimizing errors from this source. The first is the obvious one of preheating the gases entering the system so as to eliminate as far as possible the thermal gradient near the surface of the melt. The second is based upon Gillespie's[7] simplified treatment of the phenomenon which showed that the thermal separation is diminished by admixture of a gas of high molecular weight. According to this theory the error in log K_1 should be proportional to the reciprocal of the mean square root of the molecular weight of the gas. Fig 3 shows the results of a detailed experimental study[6] at 1563°C using three degrees of preheat, the apparent value of log K being plotted against the reciprocal of the mean square root of the molecular weight. From the data it was concluded that the error is eliminated by adequate preheating and greatly minimized by addition of a heavy gas. The average value using the highest, and apparently adequate, preheat agreed with results obtained at lower preheat by extrapolation to infinite molecular weight. In later experiments, including all those made above 1563°C, the preheater was operated at the same apparent temperature as the melt, corresponding to the highest preheat of Fig 3, and argon was added in the approximate ratio 4:1.

TEMPERATURE MEASUREMENTS

All temperature measurements were made by means of a disappearing-filament-type optical pyrometer sighted on the clean surface of the melt. The following is a brief description of the calibration of this method, the details of which are published elsewhere.[8] Two optical pyrometers were calibrated against a standard instrument using a tungsten strip filament lamp. A special beryllia crucible was constructed having a reentrant tube in the bottom which provided a small "black body" at the temperature of the molten metal contained in the crucible. This crucible filled with liquid iron was held in the furnace under exactly the same conditions as those used in equilibrium determinations. Simultaneous temperature readings were made on the metal surface and on the "black body" using duplicate windows and prisms and occasionally exchanging the positions of the two optical pyrometers.

Similar calibrations were carried out using a thermocouple instead of the lower optical pyrometer, the bead of the couple being inserted into the reentrant tube. For temperatures up to 1650°C a platinum-platinum-rhodium couple was employed; this was checked before and after use at the melting point of palladium. For higher temperatures extending to 1930°C an independently calibrated tungsten-molybdenum couple[9] was used. The resulting calibration curve which was used throughout this study is shown in Fig 4. The estimated uncertainty in temperature measurement is less than ±5°C at the lowest and slightly greater at the highest temperatures.

Experimental Procedure

The charge consisted of about 73 g of electrolytic iron which had been previously cleaned, pickled, washed and dried. This was held in a crucible of high-purity alumina. The whole system including the furnace was flushed out with hydrogen for about an hour. The saturator, the water bath and connecting tubing were brought to the desired temperatures.

Since the object of this series of experiments was to determine the effect of temperature upon the Fe-H_2-O equilibrium, it was necessary to let the various melts attain equilibrium at different temperatures, the range covered being from 1563° to 1750°C. Frequent temperature measurements were made and in general these did not deviate more than ±3°C from the desired value. The optical pyrometer was occasionally checked against the melting point of iron. The flow rates were adjusted to give an argon-to-hydrogen ratio of approximately 4:1 in all heats.

Preliminary runs had demonstrated that under the experimental conditions equilibrium in the reaction of hydrogen with oxygen dissolved in liquid iron was attained within fifteen minutes. All heats were continued for a minimum of forty-five minutes under steady conditions after which the metal was cooled as rapidly as possible.

To increase the rate of solidification, attempts were made to quench the melt directly into water at the end of the heat. A deep tank was arranged so that the water level was above the bottom of the furnace tube, thus excluding air, and the entire furnace bottom with the crucible and its supports was dropped into the water. The resulting ingots were mostly irregular and unsound and of very high oxygen content. Substitu-

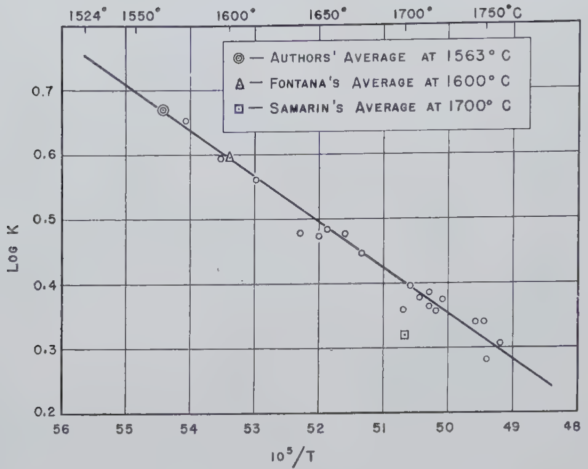

FIG 5—Effect of temperature upon the equilibrium constant

$$K_1 = \frac{p_{H_2O}}{p_{H_2} \times \% \text{ O}}$$

tion of chlorinated biphenyl for water resulted in a high-carbon ingot. The method finally adopted was to lower the melt into the cold part of the furnace, simultaneously cutting off the preheater and increasing the rate of flow of argon. Solidification occurred in five to fifteen seconds.

Most of the ingots were sound with very little or no porosity. The ingots were cut into pie-sections with a hacksaw. Grinding and pickling were used to clean the samples which were analyzed for oxygen by the vacuum fusion method. This method gives the total oxygen content of the sample and includes all the oxygen which was in solution in the melt and any oxide particles which may be entrapped in the specimen. Microscopic examination showed that the ingots were fairly clean and contained no appreciable amount of foreign oxides.

Experimental Results

The series of experiments at 1563°C which have been discussed in connection with thermal diffusion lead to a value of K_1 at that temperature of 4.68 ± 0.15. Results at higher temperatures are shown in Table 1. It is to be noted that the oxygen content of all samples is far below the saturation value in the liquid and hence there was little chance for loss during cooling. There was no visible evidence of ejection of oxide and no marked segregation in the ingots examined microscopically. Oxygen analyses were usually duplicable within ± 2 pct; in the five cases of larger deviation it is uncertain whether the cause was analytical error or actual segregation.

The results are plotted in Fig 5 in which are also shown the average values at 1600° and 1700°C reported respectively by Fontana[1] and by Samarin.[2] The best line through the data is represented by the equation:

$$\log K_1 = 7050/T - 3.17$$

This agrees very closely with Fontana's average but deviates from that of Samarin by about 18 pct in the value of K at 1700°.

Thermodynamic Calculations

COMPARISON WITH DATA ON FE-C-O SYSTEM

From the equation given above for the temperature dependence of K_1 we obtain the following for the change in free energy:

$$H_2\,(g) + \underline{O} = H_2O\,(g);$$
$$\Delta F^\circ = -32{,}250 + 14.50T \quad [1a]$$

The free energy change in the similar reaction of carbon monoxide with dissolved oxygen to form carbon dioxide is obtained from this with the aid of the free energies of the four gases involved. The data given in "Basic Open Hearth Steelmaking"[10] are in excellent agreement with the most recent compilation of the National Bureau of Standards.[11] From them we find for the water-gas reaction:

$$H_2\,(g) + CO_2\,(g) = H_2O\,(g) + CO\,(g);$$
$$\Delta F^\circ = +6380 - 6.22T \quad [3a]$$

When this is subtracted from Eq 1a the result is:

$$CO\,(g) + \underline{O} = CO_2\,(g);$$
$$\Delta F^\circ = -38{,}630 + 20.72T \quad [2a]$$

Several investigators have studied this equilibrium but it is only the results at very low carbon content that can be directly compared with the equation. The data of Marshall and Chipman[5] and of Vacher[3] for carbon contents below 0.02 pct are shown in Fig 6. The straight line represents the equilibrium constant calculated from Eq 2a which is given by the expression:

$$K_2 = \frac{p_{CO_2}}{p_{CO} \times \% \text{ O}}; \log K_2 = +8440/T - 4.53 \quad [2b]$$

It is noted that the calculated line falls within the limits of experimental uncertainty at all temperatures and in fact represents the experimental data very satisfactorily. The precision of the data for the Fe-C-O system is not as good as that for the steam-hydrogen equilibrium so that the agreement should be recorded only within limits of about ±0.07 in log K_2. This represents rather good agreement for high temperature data.

FREE ENERGY OF OXYGEN IN IRON

The free energy of formation of water vapor is given by the equation:[10]

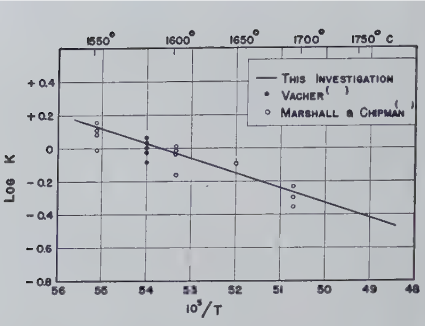

FIG 6—Effect of temperature upon the equilibrium constant

$$K_2 = \frac{p_{CO_2}}{p_{CO} \times \% \text{ O}}$$

Table 1 . . . Equilibrium Data on Reaction of Steam with Liquid Iron

Heat No.	$\frac{p_{H_2O}}{p_{H_2}}$	Metal Temp. °C	Oxygen Percent	K
65	0.1051	1574	0.0234	4.49
66	0.1040	1595	0.0265	3.92
67	0.1042	1650	0.0350	2.98
68	0.1039	1700	0.0456	2.28
87	0.1052	1615	0.0291	3.64
88	0.1052	1640	0.0350	3.01
89	0.1053	1720	0.0464	2.27
90	0.1053	1752	0.0552	1.91
103	0.1039	1665	0.0347*	3.0
104	0.1040	1704	0.0419	2.49
105	0.1040	1724	0.0438	2.37
106	0.1040	1750	0.0476	2.18
124	0.1042	1760	0.0516*	2.02
128	0.1385	1745	0.0632	2.18
300	0.1052	1716	0.0432*	2.43
301	0.1060	1716	0.0457*	2.31
140	0.0977	1710	0.0411*	2.38
141	0.0982	1655	0.0324	3.03
142	0.0984	1675	0.0352	2.79

* Average deviation about 0.0020; in all other cases less than 0.0006

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) = H_2O\,(g);$$
$$\Delta F^\circ = -60{,}180 + 13.93T \qquad [4]$$

When this is combined with Eq 1a we have:

$$\tfrac{1}{2}\,O_2\,(g) = \underline{O};$$
$$\Delta F^\circ = -27{,}930 - 0.57T \qquad [5]$$

FREE ENERGY OF LIQUID FERROUS OXIDE

The liquid oxide phase which exists in equilibrium with solid or liquid iron has a composition represented by the formula Fe_xO where the value of x is a function of temperature and, in the range considered here, lies between 0.96 and 0.99. The free energy of this equilibrium phase per gram atom of oxygen is obtained from its solubility in liquid iron and Eq 5. Its solubility[12,13] is represented by the expression:

$$\log \%\, 0 = -6320/\mathrm{T} + 2.734 \qquad [6]$$

This may be paraphrased by the equation:

$$Fe_xO\ (liq.) = x\ Fe\ (liq.) + \underline{O};$$
$$\Delta F^\circ = 28{,}900 - 12.51T \qquad [6a]$$

which, with Eq 5, gives:

$$x\ Fe\ (liq.) + \tfrac{1}{2}\,O_2\,(g) = Fe_xO\ (liq.);$$
$$\Delta F^\circ = -56{,}830 + 11.94T \qquad [7]$$

This is equivalent to the partial molal free energy of formation of FeO in the liquid oxide of equilibrium composition. From this the oxygen pressure of oxygen-saturated liquid iron is:

$$\log p_{O_2} = -24{,}850/T + 5.22 \qquad [7a]$$

COMPARISON WITH DATA OF DARKEN AND GURRY

The oxygen pressure of oxygen-saturated iron may be calculated also from the experimental data of Darken and Gurry.[14] These investigators have found the ratio p_{CO_2}/p_{CO} in equilibrium with iron and iron oxide over a wide range of temperatures, the pertinent values being reproduced in Table 2. From the known free energies of the several gases[11] we have:

$$CO\,(g) + \tfrac{1}{2}\,O_2\,(g) = CO_2\,(g);$$
$$\Delta F^\circ = -66{,}560 + 20.15T \qquad [8]$$

$$K_8 = \frac{p_{CO_2}}{p_{CO} \times p_{O_2}^{1/2}};\ \log K_8 = +14{,}550/T - 4.405 \qquad [8a]$$

Values of K_8 are included in Table 2. From these data the logarithm of the oxygen pressure is found as given in the fifth column. The sixth shows the same quantity computed from Eq 7a.

Table 2 . . . Computation of the Oxygen Pressure of Oxygen-Saturated Iron

Temp. °C	$\frac{p_{CO_2}}{p_{CO}}$	$\log \frac{p_{CO_2}}{p_{CO}}$	log K_8	log p_{O_2} (D and G)	log p_{O_2} (Eq 7a)
1371	0.282	−0.550	4.447	−9.99	
1524	0.208	−0.682	3.690	−8.74	−8.61
1575	0.194	−0.713	3.470	−8.37	−8.24
1600	0.187	−0.728	3.363	−8.18	−8.05

The discrepancy between these two series of computed oxygen pressures is very small.* It is, however, a real discrepancy since the difference is greater than the apparent uncertainties in any of the subsidiary data. Perhaps the least certain of these is the solubility of oxygen in liquid iron. The data employed here are about 30 pct lower than those which were generally accepted prior to 1941.[12] However, if the older data are substituted the discrepancy becomes greater; thus the calculation upholds the lower solubility data.

It seems quite possible that in spite of all the careful calorimetric and spectroscopic work that has been done, minor errors may remain in the free energy values of the gases which would be large enough to account in part for the discrepancies found. Inconsistencies in values of the water-gas constant, K_3, have been pointed out by Darken and Gurry[14] and until these uncertainties have been removed the small discrepancy shown in Table 2 should be no cause for worry. We may conclude then that the present data are in good agreement with the requirements of the oxygen solubility of Taylor and Chipman and the equilibrium data of Darken and Gurry.

Summary

An experimental study has been made of equilibrium in the reaction of hydrogen with oxygen in liquid iron in the temperature range 1563°–1760°C. The primary purpose was to secure more dependable data by elimination of certain errors which were inherent in earlier work.

Errors of thermal diffusion in the gas mixture were eliminated by preheating the entering gas stream to the temperature of the metal. A further safeguard was the admixture of pure argon with the gas stream in a ratio of about 4 to 1.

Temperature measurements were made by an optical pyrometer sighted on the clean surface of the melt. This system was calibrated in the range 1530°–1930°C against optical and thermoelectric measurements in a reentrant tube in the bottom of the crucible. This reduced uncertainties in temperature measurement to about ±5°.

The experimental results are represented by:

$$K_1 = p_{H_2O}/p_{H_2} \times \%\,\underline{O};$$
$$\log K_1 = 7050/T - 3.17$$

Related thermodynamic quantities are derived. The results confirm the oxygen solubility data of Fetters, Taylor and Chipman and are in good agreement with equilibrium data on the system iron-oxygen of Darken and Gurry.

Acknowledgments

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* It is considered that earlier discrepancies below the melting point of iron have been adequately explained by Darken and Gurry

The Use of Oxygen Enriched Air in the Metallurgical Operations of Cominco at Trail, B.C.

R. R. MCNAUGHTON,* Member AIME, T. H. WELDON,* J. H. HARGRAVE,* and L. V. WHITON*

Oxygen enriched air is being used quite extensively in the metallurgical plants of The Consolidated Mining and Smelting Co. of Canada, Limited, at Trail, B.C. The oxygen used for this purpose is a by-product from the Company's chemical plants located in the area.

Most of the ore treated in the Trail metallurgical plants comes from Cominco's Sullivan Mine at Kimberley, B.C. At Kimberley the ore is milled to produce lead and zinc concentrates which are shipped to Trail for further treatment to metal.

One section of this paper deals with the use of oxygen enriched air in the suspension roasting of the zinc concentrates. In this process the concentrate is calcined for leaching preparatory to electrolytic recovery of the zinc.

A second section of the paper describes the use of oxygen enriched air in operations at the lead smelter. There oxygen enriched air is used in the blast to the lead blast furnaces and in the slag fuming furnace which recovers the lead and zinc contained in lead blast furnace slag.

The final section of the paper outlines the precautions necessary for the safe use of oxygen enriched air in any plant operation.

The Use of Oxygen Enriched Air in the Suspension Zinc Roasters

The suspension roasting of zinc concentrate developed at Trail, B.C., has been described in AIME Vol. 121, "The Electrolytic Zinc Plant of The Consolidated Mining and Smelting Company of Canada, Limited" by B. A. Stimmel, W. H. Hannay and K. D. McBean. Since the publication of that paper, the use of oxygen enriched air in suspension roasting has been introduced as regular practice with marked advantage. The relative importance of a specific advantage may vary with changing conditions, but, in general, it may be stated that improved operation has been achieved at increased capacities.

Suspension roasting is carried out at Trail in converted standard 25 ft diam Wedge roasters. The 2nd, 3rd, 4th and 5th roasting hearths have been removed and the drying hearth covered over. Drying of the concentrate is done on the drying hearth and the 1st roasting hearth. The dried concentrate, after any lumps have been broken up in a ball mill, is fed to a single burner located in the upper part of the combustion chamber. Oxygen is introduced at the burner fan along with the gases from drying, returned combustion gases from the waste heat boiler outlet and the required amount of new air. Up to 60 pct of the concentrate settles out on the 6th roasting hearth, the rest passing out of the roaster. The product collected in the waste heat boiler is finished calcine, but the dust collected in the cyclones after the boilers is returned to the base of the combustion chamber where the sulphate is decomposed. Gases from the cyclones go to a Cottrell precipitator. The discharges from the 7th roasting hearth and the waste heat boiler are combined with the Cottrell dust to give the finished calcine.

Following small scale tests started in 1933, oxygen enriched air has been used continuously in the suspension roasting of zinc concentrate in Trail, beginning in 1937. A significant factor in promoting its use in this operation was the availability of by-product oxygen from the Company's near-by Chemical and Fertilizer Division. To-day it is standard practice at Trail to use oxygen enriched air for zinc concentrate roasting.

The most important requirement in roasting a zinc concentrate for an electrolytic plant is that the zinc in the calcine should have maximum solubility. It is also desirable at Trail that the gas produced for the manufacture of sulphuric acid should have a maximum concentration of SO_2 and that a substantial recovery of waste heat from the gas be achieved.

High solubility of zinc requires that the sulphide sulphur and zinc ferrite in the calcine be kept low. These are both functions of temperature and time, with formation of zinc ferrite also dependent on contact between the iron and zinc particles. One of the inherent advantages of suspension roasting is that minimum time and contact are achieved. The limit on temperature is imposed by the fusion point of the concentrate and not by the need to control zinc ferrite formation. Operating temperatures are normally maintained within the limits of 1725° and 1850°F. A relatively low zinc sulphate in the calcine is required at Trail, and this results from discharging the calcine from the high sulphur dioxide atmosphere at a temperature above 1600°F.

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* Manager, Metallurgical Division, Superintendent, Zinc Department, Superintendent, Lead Smelting Department, Superintendent of Development, Metallurgical Division, respectively, The Consolidated Mining and Smelting Company of Canada, Limited.

The rate of elimination of sulphur from the concentrate and the control of zinc ferrite formation depend in practice principally on the following factors: 1. The composition of the concentrate. 2. The fineness of the concentrate. 3. The temperature in the roaster. 4. The time allowed for roasting. 5. The concentration of oxygen in the roaster.

The limitations that exist to restrict the operation are: 1. The size of the combustion chamber. 2. The capacity for grinding the concentrate. 3. The supply of oxygen.

To control sulphur dioxide concentration in the gas to the Acid Plant and maintain this at a maximum consistent with the production of satisfactory calcine is a secondary objective. For normal operation without the addition of oxygen the furnace outlet gas contains 8.5 pct SO_2, which corresponds to a concentration of 9 pct SO_2 in the combustion chamber. This latter concentration has a calculated theoretical maximum for Trail operations of about 14 pct, with no oxygen enrichment.

The controls used in roasting are: 1. Measurement of temperature in the combustion chamber. 2. Analysis of the calcine for sulphide sulphur. 3. Continuous recording of the sulphur dioxide concentration in the roaster gases.

The calculated and observed advantages of the use of oxygen enriched air in the suspension roasting of zinc concentrate may be summed up as follows: 1. Increased capacity and greater flexibility of operation. 2. Increased concentration of sulphur dioxide. 3. Greater overall heat recovery. 4. Faster starting up and steadier operations.

To calculate the oxygen enrichment of the new air used in suspension roasting is of little value where recirculation of gases to the burner is practised. Therefore, only the volumes of oxygen used are given. These volumes are at 0°C and 760mm Hg. The advantages will now be considered in detail:

INCREASED CAPACITY AND GREATER FLEXIBILITY OF OPERATION

Increasing the concentration of oxygen in the furnace gases has a marked effect on sulphur elimination in the suspension roasting of zinc concentrate. This most important advantage may be made use of in several ways. For a given roaster capacity where the sulphide sulphur in the calcine being produced is not the lowest that it is possible to attain, a calcine lower in sulphide sulphur can be produced. If lower sulphide sulphur in the calcine is not required then the roaster capacity can be increased, or a coarser concentrate can be roasted. The foregoing indicates the greater flexibility of the roaster operation when oxygen is being used.

Current zinc concentrate treated at Trail is about 95 pct minus 200 mesh, and its analysis, and that of the corresponding calcine, are given in Table 1.

Table 1 . . . Typical Analyses of Normal Zinc Concentrate and Calcine

	Zinc Concentrate, Pct	Zinc Calcine, Pct
Zinc	48.5	53.8
Iron	12.2	14.2
Lead	5.0	5.2
Moisture	4.5	
Total sulphur	32.3	1.5
Sulphate sulphur		0.8
Sulphide sulphur		0.7

The increased capacities obtained with increased additions of oxygen are shown in Table 2. Oxygen volumes are given in cubic feet per minute at N.T.P. and the supply analyzes 98.5 pct oxygen.

Table 2 . . . Increased Capacities Obtained with Increased Additions of Oxygen

Rate of Roasting (tons per day)	Percent Sulphide Sulphur in Zinc Calcine with Increasing Oxygen			
	0 cfm	200 cfm	400 cfm	1,000 cfm
120	0.6	0.3	0.1	
140	1.3	0.7	0.4	
160	2.0	1.4	0.8	0.1
210		3.7	2.1	0.3

From Table 2 it will be seen that an increase of 20 tons per day is realized for each 200 cfm of oxygen. At rates above 150 tons per day it becomes necessary to provide cooling in the combustion chamber to control the temperature there. This is normally accomplished by recirculating cooled gas from the waste heat boiler outlet back into the combustion chamber. At Trail the capacity limitations for recirculation required that additional cooling at very high tonnages be obtained by spraying water into the combustion chamber. This operation was found necessary during the test using 1,000 cfm of oxygen for the rate of 210 tons per day, about 20 lb of water per min. being sprayed into the lower half of the combustion chamber.

At increased roasting rates extra air is also used with the increased oxygen. Indications are that the total oxygen supplied must be at least 50 pct in excess of the theoretical required. Although there is some increase in the excess oxygen required at the higher tonnages, this alone does not account for the increased rates of sulphur elimination. The full explanation must take into account the fact that the combustion chamber temperature tends generally to be higher at the higher rates.

INCREASED CONCENTRATION OF SULPHUR DIOXIDE

The first requisite of the roasting operation is to maintain a low sulphur in the zinc calcine. Gas strength at Trail is secondary to quality of calcine but is still important. Before installing the permanent oxygen supply for zinc roasting, it was decided to verify the effect of oxygen on gas strength. For this purpose a test was carried out at a normal roasting rate, using 140 cfm of oxygen. The increase in gas strength in the combustion chamber, as determined by the averages of a great many tests, was 0.3 units (9.0 pct SO_2 to 9.3 pct SO_2).

In appraising the long term benefit of oxygen as regards gas strength, many variables must necessarily be taken into account. Relatively large tonnages of acid are required at Trail, and, at times, this has necessitated the roasting of iron concentrate to supplement the gases from zinc roasting. Maximum theoretical gas strength is lower when roasting the pyrrhotite concentrate than when roasting the marmatitic concentrate. However, the use of oxygen in zinc concentrate roasting has assisted in maintaining high overall gas strength. At the same time it has also permitted higher tonnages of zinc concentrate to be roasted.

When allowances are made for all of the variables, there is always an inincrease in gas strength with increased oxygen, and at least as great as that obtained in the test reported above. Highest gas strengths are obtained when greatest quantities of oxygen are used to replace part of the air required for combustion.

The full range of gas composition in the combustion chamber has not yet been established by test work for comparison with theoretical requirements. In a high tonnage test the concentration of oxygen in the combustion chamber was 10.3 pct for a concentration of sulphur dioxide of 9.1 pct at the

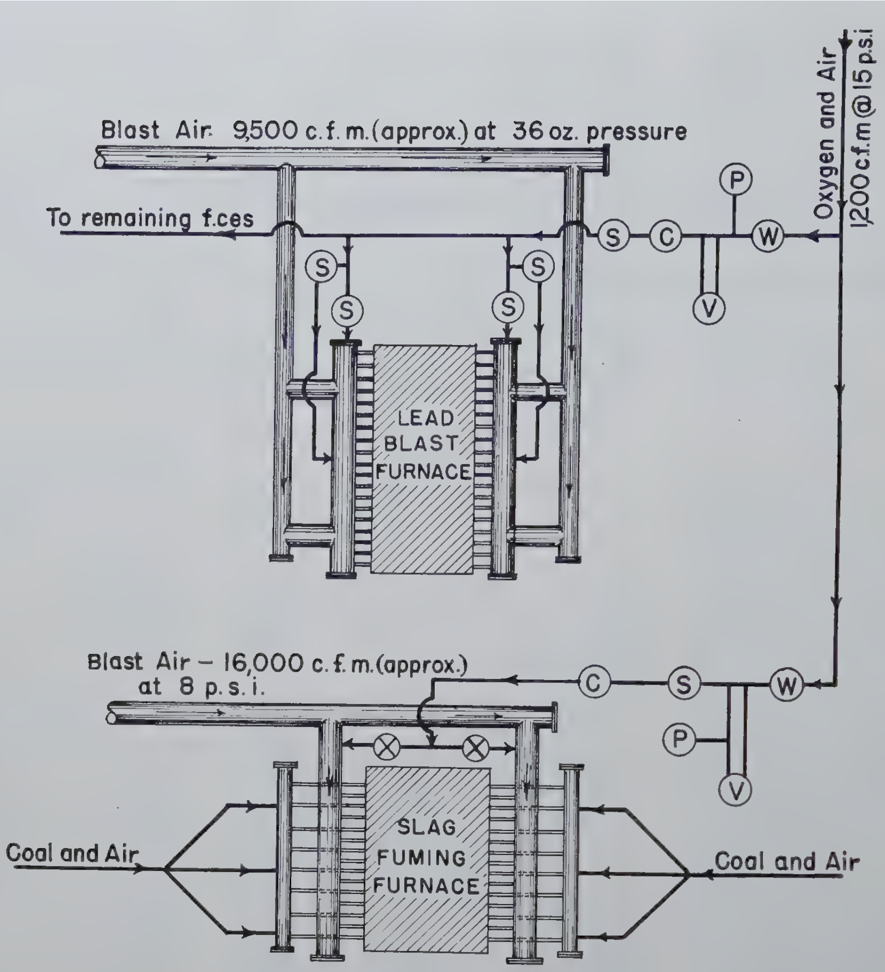

FIG 1—Smelter oxygen system.
Volumes shown are at 0°C and 760 mm Hg
X—Gate valve
C—Check valve
S—Spur gear valve
V—Volume gauge
P—Pressure gauge
W—Water trap

furnace outlet. Of course this is not the maximum sulphur dioxide concentration reached in the combustion chamber, but it does indicate satisfactory conditions for high tonnages. Any extra oxygen in the roaster gases is an advantage in converting SO_2 to SO_3 in the Acid Plant.

GREATER OVERALL HEAT RECOVERY

The use of oxygen permits greater economy in heat recovery, both through increased capacity for drying the concentrates to be roasted and in increased steam production per pound of concentrate roasted. In a test to show the increased drying rate to be gained by using oxygen at a normal roasting rate it was established that 140 cfm of oxygen increased the drying capacity by about 40 pct. The results of tests carried out to determine the greater heat recovery from the gases are given in Table 3.

Table 3 . . . Results of Tests to Determine Heat Recovery from Gases

Rate of Roasting (Tons per day)	Increase in Heat Recovery Using 400 cfm of Oxygen Pct
120	21
140	18
160	11

FASTER STARTING UP AND STEADIER OPERATION

Of less importance, but certainly a definite advantage of the use of oxygen in zinc roasting, is the greater speed that is achieved in getting the roaster up to temperature to produce satisfactory calcine. The lower temperature at which ignition of the concentrate occurs and the more rapid rise in temperature mean quicker starting after a shutdown. This results in a saving of fuel oil and minimum dilution of the roaster gases during starting up.

Fluctuations in the chemical and physical properties of the concentrates being fed, which occur particularly in treating a variety of customs concentrates, are more easily taken care of when oxygen is being used to enrich the air for combustion. The normal procedure is to maintain the oxygen supply constant and make the other necessary adjustments. The result is a much steadier operation.

SUMMARY

Tests have been carried out using up to 1,000 cfm of oxygen on one suspension zinc roaster to obtain satisfactory operation up to 210 tons per day. The suspension zinc roasters at Trail are normally supplied with about 300 cfm of oxygen per roaster. The greatest single advantage has been to increase the individual roaster capacity from 120 tons per day to 150 tons per day. Gas strengths have been increased up to 5 pct. Heat recoveries have been increased up to 15 pct with the use of oxygen.

Advantages are achieved in proportion to the actual oxygen being used. Operation may be varied to obtain the maximum of the advantage desired at a particular time. A much steadier roaster operation is achieved when oxygen is being used and the operation is more flexible.

Consideration is being given to the use of even greater quantities of oxygen. The object of this is to increase the capacity of present roasting equipment still further, and to obtain increased concentration of sulphur dioxide in the gases going to the Acid Plant for increased acid production.

The Use of Oxygen Enriched Air in the Slag Fuming Furnace and Lead Blast Furnaces

The use of oxygen enriched air has interested both ferrous and nonferrous pyrometallurgists for many years. The Trail Lead Smelter is fortunate in having available a limited supply of byproduct oxygen from the Company's Chemical and Fertilizer Division. This fact led to the institution of a test program on the use of oxygen enriched air in both the lead blast furnaces and the slag fuming furnace.

To date most of the test work with oxygen enriched air at the Lead Smelter has been carried out on the slag fuming furnace, where both throughput and zinc recovery have been notably improved. The test work on the lead blast furnaces, although not very far advanced, has indicated a definite coke-saving and much smoother furnace operation.

The compressor delivering oxygen to the Lead Smelter handles a constant volume of 1,200 cfm, which is delivered to the Smelter at 15 psi. When less than 1,200 cfm of oxygen is used, air is introduced into the compressor to make up the difference and the Smelter receives a mixture of air and oxygen. This is fed into the bustle pipes on the slag fuming and blast furnaces with suitable measuring and control devices as shown in Fig 1. All volumes are given at 0°C and 760 mm Hg. 1,000 cfm of oxygen at N.T.P. equal approximately 65 tons per day.

SLAG FUMING FURNACE TESTS

Details of construction and operation of the slag fuming furnace have been published in *Transactions* AIME 121, "Slag Treatment for the Recovery of Lead and Zinc at Trail, B. C." by R. R. McNaughton. Briefly, the furnace is 10 ft wide by 24 ft long and 10 ft high with 36 2-in. tuyeres on each side. Pulverized coal and air are blown through the slag bath where the ZnO is reduced to Zn with the temperature of the bath maintained at about 2,200°F. Above the bath the Zn is oxidized again to ZnO. The furnace gases carrying the ZnO pass through a waste heat boiler where they are cooled to 900°F. They then pass through an economizer and finally reach the baghouses at something less than 220°F.

Normally the total volume of air to the furnace is approximately 16,000 cfm at 8 psi ga. Pulverized coal is used at a rate of approximately 200 lb per min. Operation of the fuming furnace is a batch operation and the furnace charge is 55 tons of molten lead blast furnace slag analyzing 16.5 pct zinc, 20 pct silica, 10 pct lime and 28 pct iron. Until recently the standard cycle of operations was 9 blows in 24 hr or 160 min. per blow.

The rate of elimination of the zinc from the molten slag charge depends in practice principally upon the following factors: 1. The composition of the slag. 2. The temperature of the slag. 3. The concentration of CO in the gases agitating the slag.

There are limitations in the existing plant equipment that control the operation, such as: 1. The gas handling capacity of the waste heat boiler and subsequent equipment. 2. The capacity of the blower to supply blast air. 3. The working capacity of the furnace (agitation of the charge must not splash slag into the flue). 4. The cooling capacity of the water jackets (limits furnace temperature).

Altogether about 100 tests, using up to a maximum of 26.5 pct oxygen in the blast, have been carried out on the slag fuming furnace to show the effect of oxygen. Some 30 of these were averaged to give the three sets of figures given in Table 5, which are graphed in Fig 2. In Table 6 the capacity and recovery increases for 23.4 pct oxygen in the blast (500 cfm oxygen added) are shown. In these calculations an empirical figure of 81 pct is used to obtain the tons of slag discharged from the furnace in relation to the tons of slag charged.

Although there is a slight increase in coal consumption the measurement of this has not been accurate enough for comparative purposes. The small increase in steam production is relatively insignificant.

Without the addition of oxygen the slag temperature, as measured by a locally developed continuous optical temperature recorder, averaged about 2150°F. The use of oxygen has enabled temperatures slightly in excess of 2300° to be maintained. Limitations of the existing equipment prevent operation at higher temperatures.

The points of greatest interest on the curves in Fig 2 fall between blowing times of 100 and 140 min. In this range the rate of zinc elimination commences to fall off. It may be possible that the use of still greater proportions of oxygen to give slightly higher temperatures will permit the development of the operation of a continuous process. Of course, the economics of changing metal prices combined with production costs must be included in any calculations made to establish an operating program.

LEAD BLAST FURNACE TESTS

Details of operation of the lead blast furnaces at Trail have been published in *Transactions* AIME Vol. 121, "Lead Blast Furnace Practice at Trail, B. C." by G. E. Murray. The dimensions of the Trail furnaces have in some cases been altered. Therefore the significant dimensions are given in Table 4 and also the normal blast air volumes.

Table 4 . . . Furnace Dimensions

Furnace Number	9	10	11	12
Length (in.)	180	270	180	270
Width at Tuyeres (in.)	98	65	65	69
Width at Top of Shaft (in.)	120	82	82	76
Normal Blast Air Volume (cfm)	8,500	9,500	7,500	10,000

Table 5 . . . Slag Fuming Furnace—Analyses of Slags

Blowing Time (minutes)	Zinc Remaining in Slag with Oxygen Content in Blast Air of		
	20.9 %	23.4 %	24.8 %
0	16.8 %	16.9 %	16.4 %
20	14.3	13.6	13.2
40	12.1	11.4	10.8
60	10.0	9.1	8.4
80	7.9	6.9	5.9
100	6.0	4.9	3.9
120	4.3	3.3	2.6
140	3.3	2.2	1.4
160	2.9	1.6	0.9

Table 6 . . . Slag Fuming. Capacity and Recovery Increases for 23.4 Pct Oxygen in Air (500 cfm)

Oxygen—Pct in Blast Air	20.9	23.4	23.4
Length of Blows—min	160	160	133
Number blows per 24 hr	9	9	11
Slag Blown—Tons per 24 hr	495	495	605
Pct Zn. in Slag—In	16.8	16.9	16.9
Out	2.9	1.6	2.6
Tons Zn—In Slag Charged	83.2	83.7	102.3
Off in Fume	71.6	77.3	89.5
In Slag Tapped	11.6	6.4	12.8
Zn Production Increase—Tons		5.7	17.9
Pct		8	25

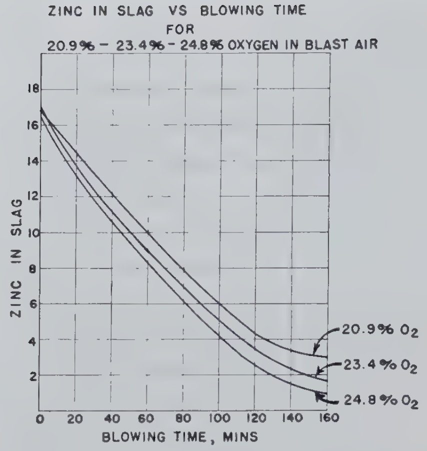

FIG 2—Effect of oxygen on slag fuming operation.

Interruptions in the supply of oxygen have made it impossible to carry through a prolonged continuous test on one blast furnace. Nevertheless the following figures will give some indication of advantages to be expected. A comparison of No. 10 blast furnace using 22.3 pct oxygen in the blast with No. 12 blast furnace using no oxygen showed a coke saving of 3.9 pct. Using 23.0 pct oxygen in the blast on No. 10 furnace and comparing the operation again with No. 12 blast furnace, the coke saving amounted to 12.1 pct. There were corresponding production increases of 20 pct and 30 pct for No. 10 furnace over No. 12. However, comparing the operation of No. 10 furnace using oxygen with its own previous operation for a comparable two months' period without oxygen, the increase in production amounted to only 15 pct for the total period it was using oxygen.

Oxygen has been valuable in blast furnace operation in preventing the formation of, or aiding to smelt out quickly, the crusts which generally form in the lower shaft or crucible. The normal time of smelting out these crusts is about 3 days, whereas the use of up to 27.5 pct oxygen in the blast enables them to be smelted out in one day or less by increasing bottom temperatures.

Although records do not indicate any marked increase in maximum furnace temperatures, slag temperatures are on the average somewhat higher and better conditions do prevail in the upper shaft to give steadier furnace operation.

To summarize the rather small amount of test work carried out on the lead blast furnaces, it can only be said that indications point to a reduction in coke requirements of about 10 pct with an increase in furnace capacity of 15 to 20 pct for an oxygen enrichment giving 23.4 pct oxygen in the blast air. The regular use of 22.1 to 25.0 pct oxygen enriched blast with occasional applications up to 27.5 pct oxygen enrichment to smelt out crusts should prove to be economic in lead blast furnace operation. For enrichments greater than the above it will probably be necessary to make alterations in furnace design to achieve best results.

CONCLUSIONS

The value of oxygen in the slag fuming operation at Trail is in increased furnace throughput and higher zinc recovery. Further development work will require modifications in furnace design. These are already under consideration. Ultimately a continuous operation may be obtained.

In the lead blast furnaces the indications are that oxygen reduces coke consumption and increases furnace capacity. This work is continuing and will do so until the limits of the present equipment are reached. Alterations in design will probably then be necessary as in the case of slag fuming.

The Precautions Necessary with the Use of Oxygen Enriched Air in Plant Operations

The use of oxygen enriched air in plant operations requires that certain precautionary measures be taken because of the following characteristics of oxygen:

1. Oil and grease may react violently with oxygen.

2. Spontaneous combustion occurs more readily in the presence of oxygen. The probability of a spark causing ignition during a static discharge is increased.

3. Oxygen accelerates combustion. It has been stated that the rate of acceleration increases rapidly up to a concentration of 40 pct oxygen with little difference noted between 40 and 100 pct oxygen.

The only positive method of preventing oxygen flow beyond a given point in a line is to insert a blind flange. It is strongly recommended that this procedure be adopted where any work is to be carried out in a system beyond a given cut-off point. Also, the system beyond this point should be completely purged of oxygen with large volumes of air.

A Thermodynamic Investigation of the System Silver-silver Sulphide

TERKEL ROSENQVIST*

Introduction

From the chemical, metallurgical, and mineralogical points of view, the importance of thermodynamic data for metal-sulphides and sulphur dissolved in molten metal has long been realized. Such data will give a basis for thermodynamic calculations of processes such as roasting and the distribution of sulphur between molten metal and slags. Furthermore, it will help us understand the chemical forces which tie sulphur to the metal and to the melt.

Thermodynamic studies of solid sulphides and the equilibria between solid sulphides and metals have been carried out in a rather large number of cases by several investigators. An excellent review of this work is given by Kelley.[1] On the other hand, very little is known about the thermodynamic properties of molten sulphides and of sulphur dissolved in molten metal. The only system which previously has been investigated in this respect is the iron/sulphur system.

The purpose of the present investigation was primarily to obtain further data for metal/sulphur melts and the system silver/sulphur was chosen, not because this system was expected to be of special interest in itself, but because the silver/sulphur system is a typical example of a metal/sulphur system. Because of the low melting temperatures, the work could be carried out without appreciable furnace and refractory difficulties. The sulphur in this system possesses a rather high escaping tendency compared to most other metal/sulphur systems. By the method employed (reaction with hydrogen to form hydrogen sulphide) this gives ratios P_{H_2S}/P_{H_2} up to 0.30, which may be determined accurately.

Thermodynamic investigations of the heterogeneous reaction $Ag_2S + H_2 \rightarrow 2Ag + H_2S$ have previously been carried out by Pelabon,[2] Keyes and Felsing,[3] Jellinek and Zakowski,[4] Watanabe,[5] and Britzke and Kapustinsky.[6] Their results are in rather poor agreement.

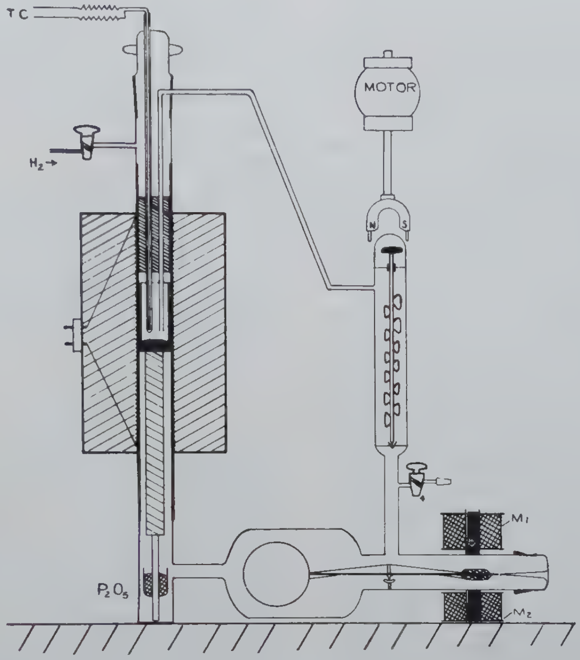

FIG 1—Apparatus for studies of gas-metal equilibria.

Experimental Part

PRINCIPLE

In the present investigation the escaping tendency of sulphur from the condensed phase was determined by the reaction:

$$S + H_2 = H_2S$$

The ratio P_{H_2S}/P_{H_2} is at constant temperature, directly proportional to the escaping tendency of sulphur and to its chemical activity in the condensed phase. (This ratio will subsequently be denoted by H_2S/H_2.) From this ratio and its variation with temperature and with change in the composition of the condensed phase, thermodynamic quantities such as free energy and heat of reaction can be derived. The apparatus used is shown in Fig 1. The silver/sulphur alloy was placed in a crucible inside a refractory tube and mounted inside the furnace to the left. The tube was a part of a closed, gas-tight system in which the gas mixture could circulate until equilibrium was established. Circulation was maintained by the glass propeller to the right, driven by an external magnet, and promoted by the chimney action of the furnace. The gas passed up through the furnace, down into the crucible where it came in contact with the alloy, passed rapidly up through a narrow tube and out of the hot zone.

After equilibrium was established between the gas and the condensed phase, the composition of the gas mixture was determined from its density. In its circulation, the gas mixture passed through a chamber (lower right on Fig 1) containing a buoyancy-balance, where the density of the gas was determined by magnetic balancing. From the measured density,

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* Instructor, Institute for the Study of Metals, University of Chicago.

[1] References are at the end of the paper.

corrected for pressure and temperature, the H_2S content, and consequently the H_2S/H_2 ratio were determined. For the gas compositions in question (1–25 pct H_2S) this method is more accurate than the usual chemical analytical methods for H_2S determination. The method further has the advantage compared with chemical analysis, that no gas is removed from the system during the determination. Thus, the progression of the gas-metal reaction could be followed by means of a large number of density determinations, until constant density indicated attainment of equilibrium. This would take from 4 to 5 hr, but the runs were always continued to a total of 12 hr. Prolonged heatings for another 24 hr, which were tried on some samples, produced no further change in the gas composition.

The equilibrium ratios could be determined for any number of temperatures during one heating, without need for withdrawal of gases for analysis or replenishment of the alloy.

After the end of each run, the sulphur content of the alloy was determined by analysis. In order to avoid any back reaction with the gas during cooling, the system was always evacuated to a few mm pressure after the last measurement had been taken (usually at about 1000°C) and cooled in vacuum.

For analysis, the alloy was oxidized by solution in hot concentrated nitric acid and the sulphate thus formed precipitated and weighed as $BaSO_4$ in the usual way.*

EXPERIMENTAL DETAILS

Materials

The silver/sulphur alloys used were made from electrolytically refined silver, 99.99 pct pure, and sublimed sulphur. Silver sulphide was prepared by heating together stoichiometric amounts of the elements in evacuated and sealed quartz tubes at a temperature of 500–700°C. This reaction was always complete. Silver/sulphur alloys of different compositions were obtained when weighed amounts of silver and silver sulphide were mixed and heated together during the run.

Thermocouple

For all temperature readings, a Pt-13 pct PtRh thermocouple was used. This thermocouple was calibrated by means of the melting points of antimony, silver, gold, and palladium—the last two by the wire-bridge method. (A short wire of the calibration metal is inserted in the thermocouple junction and heated until the wire melts, breaking the circuit.)

Furnace

A platinum resistance furnace was used. In order to obtain constant temperature for a period of time, the furnace was fed with current from a constant voltage transformer, and the input was regulated with a variable transformer. In this way, a temperature constancy of ±2.5°C was obtained for days. This is somewhat poorer than by a good temperature controller, but is more dependable in the long run. In the table of experimental results, the temperature is always given to the nearest 5°C.

Refractories

A tube of mullite was used for the main reaction tube. It proved to be absolutely vacuum tight during the entire work (which covered more than 30 runs over a period of about one year). The thermocouple tube and the outlet tube for the gas were of high grade porcelain, approximating mullite in their composition. However, leaks soon developed in the thermocouple tube. Therefore, an inner thermocouple tube of vitrous quartz, sealed gas tight to the porcelain tube, was used. After a couple of runs this quartz tube devitrified and had to be replaced.

A plug of alundum was cemented on to the thermocouple and outlet tubes and acted as a baffle to prevent heat radiation and gas convection to the upper part of the system.

The crucibles were of sintered high purity aluminum-oxide, (Pure-oxide from Norton Co.) free of silica. They stood up well and no chemical reaction seemed to have taken place between the crucible and the gas, or between the crucible and the alloy.

With exception of the crucibles, all other refractories contain some combined silica which gradually would be reduced by the gas at high temperatures. The refractories were therefore reduced with hydrogen at 1300°C before they were used. Nevertheless, some reduction always occurred during the runs. The water-vapor thus formed was absorbed in P_2O_5 placed in a small cup in the cold zone of the system.

Contamination of the alloy with silicon from the refractories is a usual source of error in work of this kind; therefore a few of the alloys were examined spectroscopically for silicon. The alloys were found to be free of silicon.

The Buoyancy Balance

The buoyancy balance is in principle similar to what is earlier described by Stock,[7] but certain changes have been made. It was built primarily of Pyrex glass. The beam was built of fine tubes of Pyrex glass with fine porcelain tubes fused on internally for increased rigidity. The bulb was blown of Pyrex glass to about 230 cm³ and weighed less than 20 g. The counterweight was a Pyrex tube in which some lead was fused together with a small sheet of transformer iron. Eventually this tube was evacuated and closed so that the reaction gas did not come in direct contact with any metal parts. For the same purpose, the knife edge and the support for the balance were made of mullite porcelain, ground to shape and fused in place with uranium glass. The balance was operated by means of the external magnet M_1 (Fig 1) which contained a core of transformer iron. A current was passed through the magnet coil until a fine needle on the counterweight was just level with a corresponding stationary needle. In order to reduce the effect of magnetic hysteresis, the balanced position was always approached from a highly magnetized state, and in such a way that oscillation of the balance in the magnetic field was avoided. In this way, the effect of magnetic hysteresis was reduced to considerably less than 1 pct.

Between the readings, the balance was kept steadily in place by passing current through the lower magnet M_2. This current, as well as the current for the propeller, was shut off the moment a density reading was taken.

The balance was so made that it was just balanced, without any magnetic influence, for a gas density slightly less than pure hydrogen at atmospheric pressure. This offers the widest operating range and greatest sensitivity for low H_2S contents.

The balance was calibrated by means of gases of known density. As such, dry air, nitrogen, helium and hydrogen were used. By varying the pressure of the calibration gas, a wide range of densities could be covered. The density of the gas was plotted as a function of the current in the magnet. The calibration was tested on known mixtures of hydrogen and hydrogen sulphide and a satisfactory agreement with the calibration was found.

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* Thanks are due to the analytical laboratory of the Institute and particularly to Mr. R. E. Fryxell for the chemical analyses.

From the observed density of the gas mixture, the average molar weight M of the gas was derived. This gives the percentage of H_2S in the gas and the H_2S/H_2 ratio:

$$\%H_2S = \frac{M - 2.016}{32.06} 100$$

and

$$\frac{H_2S}{H_2} = \frac{M - 2.016}{34.08 - M}$$

The sensitivity of the balance in itself was about 0.3 mg corresponding to about 0.1 vol. pct of hydrogen sulphide. However, because the balance had a tendency to change position on its support, mainly due to vibration from the gas propeller, the calibration shifted somewhat back and forth. The balance was therefore recalibrated between every run. Nevertheless, the practical accuracy, as far as one could judge from parallel runs, would be about 0.2–0.3 pct H_2S which, for a gas of 20–30 pct H_2S, would represent a relative accuracy of 1 pct.

SOURCES OF ERROR

The value we are interested in is the ratio H_2S/H_2 of the gas when it is in equilibrium with the condensed phase in the hot zone. But the gas was analyzed at room temperature. Thus the question arises whether or not this analysis is representative of the hot gas.

Two different factors may tend to change the composition of the gas on cooling:

1. The gas mixture, in the hot zone, will hold a small amount of sulphur vapor as S_2 gas according to the equilibrium:

$$2H_2S \rightleftarrows 2H_2 + S_2 \text{ (endothermic)}$$

In the present work, the sulphur pressure in the hot zone, P_{S_2}, may be as high as 5 mm Hg.

The sulphur vapor will be carried along with the gas flow and on cooling, will react with H_2 to give H_2S. This will increase the ratio H_2S/H_2 in the cooled gas. That this reaction actually occurred is evident from the fact that no condensation of sulphur was observed in the cold part of the system.

In order to obtain the gas ratio H_2S/H_2 in the hot zone, the value observed in the cold zone must therefore be corrected. This correction has been disregarded by most investigators who previously have done work of this kind. But it can be shown that in extreme cases it may attain 10 pct.

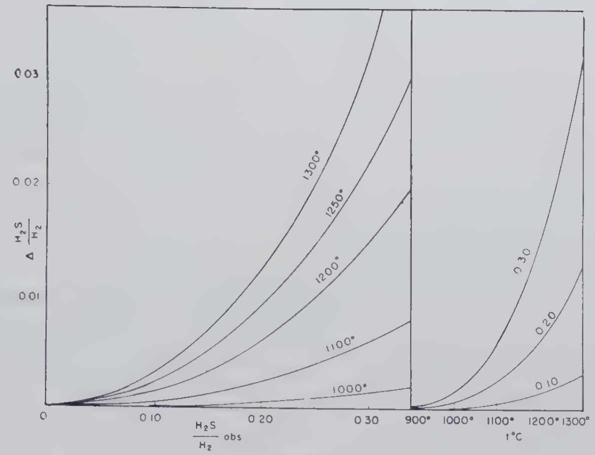

FIG 2—Correction curves for H_2S/H_2.

The curves to the left give the correction as a function of $H_2S/H_{2(obs)}$ for five different temperatures. The curves to the right give the correction as a function of temperature for three different values of $H_2S/H_{2(obs)}$.

If the correction should be done arithmetically on the basis of the observed gas ratio and the equilibrium constant for the reaction $2H_2S \rightarrow 2H_2 + S_2$, it would involve solving a third order equation. However, it can be done rather easily by a graphical method.

From a series of arbitrarily chosen values for the gas ratio in the hot zone, called $H_2S/H_{2(corr)}$, the equilibrium concentration of S_2 vapor was calculated. On cooling, each S_2 molecule combines with $2H_2$ molecules and gives $2H_2S$ molecules. Consequently, the expected gas ratio at room temperature, $H_2S/H_{2(obs)}$, could be calculated. The difference

$$\Delta H_2S/H_2 = H_2S/H_{2(obs)} - H_2S/H_{2(corr)}$$

was then plotted graphically against $H_2S/H_{2(obs)}$. When this was done for a series of temperatures, (for example, 1000, 1100, 1200, 1250 and 1300°C) a series of smooth curves were obtained (see Fig 2). From these curves, the correction for any experimental $H_2S/H_{2(obs)}$ could be made with sufficient accuracy. It will be seen that for temperatures below 1000°C and also for small H_2S/H_2 ratios, the correction is negligible.

2. The effect of thermal diffusion may cause considerable errors.

It was shown by Soret (1881) that a homogeneous aqueous solution, in response to a thermal gradient, develops differences in concentration in the cold and hot zones. It was later shown by Emmett and Schultz[8] that the same effect occurred in mixtures of gases having different densities, and that this caused considerable errors in studies of gas-metal equilibria if performed in a *static* system. For the equilibrium of metal-metal oxides with an H_2O-H_2 atmosphere, the error in the equilibrium constant could be as much as 40 pct. Chipman and Dastur[9] have shown that the same effect arises in a *dynamic* system if the gas was insufficiently preheated before it reached the condensed phase.

In the present work, special precautions have been taken to avoid this source of error. The gas must be expected to be sufficiently preheated before it reaches the metal as it passes from below, through the resistance heated furnace, up outside the crucible and then down into it.

The fact that the gas circulates at a rather high rate (about 30 to 50 cm^3 per min.) prevents inhomogeneity when going from the hot to the cold zone. No appreciable change occurred in the gas composition when the flow rate was varied by a factor of two (by speeding up or slowing down the propeller) indicating that the flow rate was sufficient to eliminate the thermal diffusion. That inhomogeneity would occur if there were no circulation, was shown in one experiment: A "dynamic equilibrium" was established at 1055°C (Run 17) and a gas ratio of 0.218 (corr), 0.220 (obs), was found. Then the circulation was arrested by turning the ground joint top of the apparatus. After the system had been left overnight at the same temperature, a gas ratio of 0.325 (obs) was measured. This is about 50 pct higher than the "dynamic composition." The original value was reproduced when the circulation was started.

EXPERIMENTAL RESULTS

After a number of preliminary runs (which were made to work out the

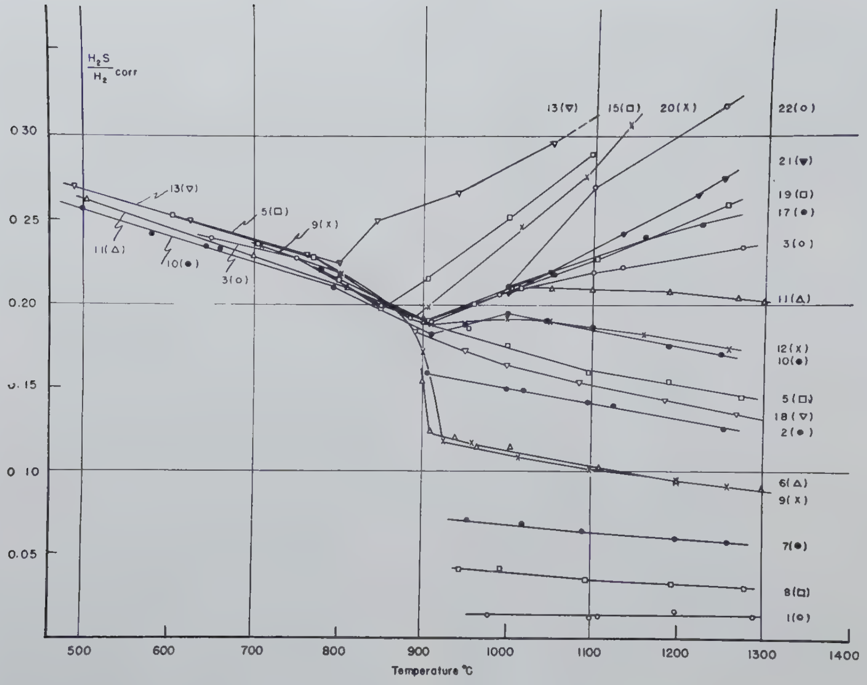

FIG 3—Ratio H_2S/H_2 for runs 1–22.

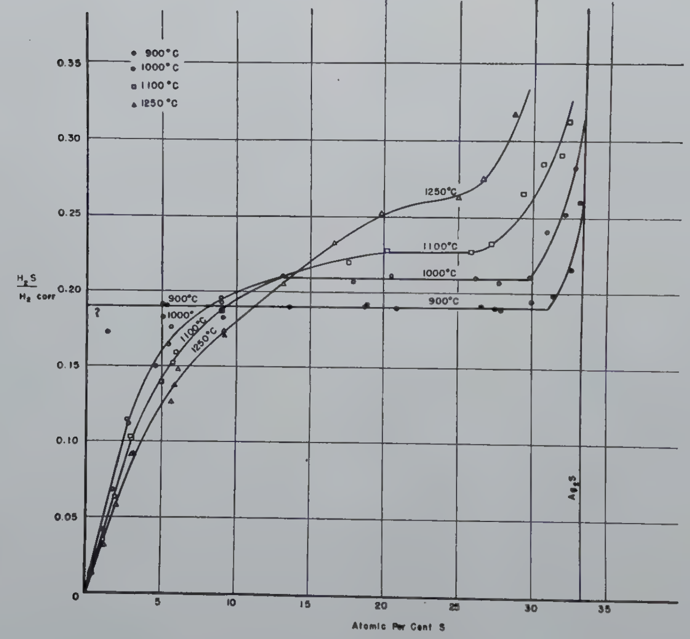

FIG 4—Equilibrium ratios as a function of composition of the alloy.

method) 22 main runs were done with sulphur contents varying from 0.4–33.3 at. pct (0.14–13.9 wt pct). In most of these runs the initial gas was pure hydrogen. However, some runs were started with an initial H_2S/H_2 mixture of a ratio 0.25, thus approaching the equilibrium from the high side. These runs gave values in agreement with the rest of the work.

In Table 1, the runs are tabulated in the order they were made; likewise are the readings at different temperatures listed in the sequence in which they were carried out. In the first column is given the number of the run, the weight of the alloy, and the volume of the gas. The volume is reduced to 760 mm pressure and 0°C. The composition of the silver/sulphur alloys is given in atomic per cent. The compositions which are *italicized* are the ones obtained by chemical analysis. The compositions at other temperatures of the same run are recalculated from the analytical data, on the basis of the change in gas composition with temperature, the weight of the alloy, and

Table 1 . . . Experimental Runs

Run No Alloy Weight Gas Volume (in Liter)	t°C	Sulphur Content	Ratio H_2S/H_2
		At. Pct	Corrected
No 1	1100	0.47	0.013
30.22g	1200	0.47	0.016$_5$
1.40 l	1290	0.45	0.014
	1105	0.47	0.013$_5$
	980	0.46	0.013$_5$
	1200	*0.47*	No reading made
No 2	905	4.13	0.159
8.84g	1000	4.66	0.149$_5$
1.36 l	1095	5.03	0.142
	1255	5.70	0.126
	1115	5.10	0.140
	1010	*4.66*	0.149
No 3	650	17.0	0.239$_5$
9.18g	750	17.5	0.227$_5$
1.35 l	850	18.6	0.199
	910	18.9	0.190
	990	18.2	0.206
	1135	17.5	0.222$_5$
	1275	16.6	0.234
	1100	17.6	0.219$_5$
No 4	800	5.2	0.216
19.18g	900	5.2	0.192
1.33 l	Runs at higher temperature failed because crucible broke		
No 5	605	4.23	0.253
21.73g	705	4.52	0.236
1.38 l	770	4.68	0.227$_5$
	885	5.40	0.191$_5$
	955	5.49	0.186
	1095	6.02	0.160
	1190	6.08	0.153$_5$
	1270	6.24	0.144
	1000	*5.68*	0.176
No 6	900	2.05	0.154
29.04g	910	2.57	0.124
1.38 l	940	2.64	0.120
	965	2.72	0.114$_5$
	1110	2.96	0.102
	1200	3.09	0.093$_5$
	1300	3.15	0.089
	1005	2.74	0.114$_5$
No 7	955	1.83	0.070$_5$
30.18g	1090	1.94	0.064
1.38 l	1200	2.01	0.060
	1260	2.05	0.057$_5$
	1020	*1.85*	0.068$_5$
No 8	945	1.19	0.041
30.48g	1095	1.30	0.035
1.38 l	1195	1.35	0.032$_5$
	1280	1.37	0.030$_5$
	995	*1.17*	0.041$_5$
No 9	710	0.16	0.235$_5$
20.36g	805	0.50	0.218$_5$
1.36 l	900	1.48	0.171$_5$
	925	2.68	0.118$_5$
	960	2.71	0.117
	1100	3.06	0.101$_5$
	1200	3.22	0.093$_5$
	1260	3.23	0.092
	1015	*2.90*	0.108$_5$
No 10	660	8.53	0.232$_5$
29.12g	580	8.39	0.241$_5$
1.36 l	430	equilibrium was not reached	
	500	8.20	0.256$_5$
	652	8.48	0.235
	795	8.83	0.210
	910	9.22	0.182
	950	9.13	0.188
	1045	9.07	0.190$_5$
	1100	9.10	0.187
	1190	9.25	0.175
	1250	9.25	0.170$_5$
	1000	*9.01*	0.195
No 11	700	13.3	0.229$_5$
29.63g	810	13.4	0.209$_5$
1.36 l	505	12.8	0.262
	900	13.7	0.190
	1050	13.4	0.210$_5$
	1190	13.4	0.207$_5$
	1270	13.4	0.204
	1300	13.4	0.201$_5$
	1100	13.4	0.209$_5$
	1005	13.4	0.210$_5$
No 12	910	9.16	0.188
29.12g	950	9.18	0.187
1.34 l	1050	9.13	0.190
	1160	9.18	0.182$_5$
	1260	9.24	0.174
	1000	*9.11*	0.192
No 13	490	33.1	0.270
15.42g	625	33.4	0.249$_5$
1.33 l	762	33.7	0.230
	800	33.7	0.225
	845	33.3	0.250

Table 1 . . . (Continued)

Run No Alloy Weight Gas Volume (in Liter)	t°C	Sulphur Content	Ratio H_2S/H_2
		At. Pct	Corrected
	940	33.1	0.267
	1050	32.6	0.295_5
	(1100) (extrapolated)	(32.4)	(0.312_5)
No 14	780	17.4	0.221
24.63g	910	17.8	0.192
1.37 l	950	17.7	0.200
	Runs at higher temperature failed because crucible broke		
No 15	800	32.68	0.215
27.89g	905	32.68	0.215_5
1.35 l	1095	31.95	0.289_5
	850	32.81	0.198_5
	1000	*32.32*	0.252_5
No 16	905	27.6	0.190
29.15g	Runs at higher temperature failed because crucible broke		
1.37 l			
No 17	905	20.96	0.189
23.87g	1055	20.51	0.218
1.38 l	1160	20.15	0.240_5
	1225	20.00	0.247_5
	1000	*20.59*	0.211_5
No 18	890	5.21	0.183_5
26.41g	950	5.41	0.173
1.38 l	1085	5.71	0.154
	1185	5.90	0.142_5
	1270	6.00	0.134
	1000	*5.56*	0.164
No 19	905	26.7	0.191
14.75g	1105	25.9	0.226_5
1.39 l	1180	25.4	0.246_5
	1255	25.0	0.259
	1015	26.3	0.209
No 20	900	31.5	0.198_5
28.10g	1090	30.7	0.276_5
1.36 l	1140	30.4	0.307_5
	1015	31.0	0.247
No 21	905	27.95	0.189
23.31g	1135	27.25	0.242_5
1.39 l	1220	26.95	0.265
	1050	27.55	0.219_5
	1250	26.70	0.275
	1000	*27.85*	0.206
No 22	850	30.07	0.200_5
26.67g	895	30.15	0.194
1.33 l	1100	29.39	0.265_5
	1250	28.80	0.317
	965	30.02	0.206
	1000	*29.98*	0.210_5

the volume of the gas. For a few runs in the medium composition range, the alloys were not analyzed but their sulphur contents calculated from their original composition by correcting for the sulphur losses to the atmosphere. These values are given with one decimal place less than the others and are not underlined.

In Fig 3 is plotted the gas ratio, $H_2S/H_{2(corr)}$, as a function of temperature for all runs.

Fig 4 gives the variation of the gas ratio with composition of the alloy for four different temperatures: 900, 1000, 1100, and 1250°C. When no experimental value existed for the exact temperature, the points were obtained by interpolation from Fig 3.

In Fig 5 is plotted log H_2S/H_2 against 1/T for a number of compositions as they are taken from Fig 4. It is obvious that the data given in Fig 5 do not represent the experimental data directly, but are obtained by interpolating between them. Therefore they give an idealized picture where experimental scatterings are smoothed out. On the other hand, they are derived from a large number of experimental data, and no appreciable error should be introduced by this procedure.

Discussion of Results

COMPARISON WITH THE RESULTS OF PREVIOUS INVESTIGATORS

The heterogeneous equilibria between phases rich in Ag_2S and Ag have been investigated by Pelabon,[2] Keyes and Felsing,[3] Jellinek and Zakowski,[4] Watanabe,[5] and Britzke and Kapustinsky.[6] Their data are plotted in Fig 6, together with the present data for the same heterogeneous equilibria.

The data of the previous investigators are derived by using different techniques. Pelabon as well as Keyes and Felsing established the equilibrium composition of the gas mixture inside a container kept at constant high temperature. The gas mixture was then quenched to room temperature and analyzed. Pelabon quenched the entire container (a quartz tube); Keyes and Felsing withdrew the gas from the hot zone into an evacuated burette. As seen, there is poor agreement between their values. It should be noted that Pelabon worked with rather small gas volumes and that an inaccuracy in the chemical analysis is possible. Keyes and Felsing's values are the averages of a series of parallel runs which in themselves deviated as much as 10 pct from the mean value.

Watanabe established his gas equilibrium in the hot end of a tube, and withdrew gas for analysis from the cold end. It is obvious that this leads to inhomogeneity of the gas by thermal diffusion, and that his values for the gas-ratio must be too high. In fact the value which in the present investigation was obtained by closing off the circulation, and which in Fig 6 is denoted by an *, agrees with what one should expect by extrapolation from Watanabe's data.

The data of Jellinek and Zakowski run rather parallel to those of the present investigation but are about 25 pct higher. Their method was a dynamic one in which the gas passed only once over the condensed phase. In order to correct for incomplete reaction, they made several runs of different flow rates, and the equilibrium compositions were obtained by extrapolation to zero flow rate. By this extrapolation they actually introduce to some extent, the effect of thermal diffusion. Their experimental runs were made at flow rates from 6 to 1 cm³ per min., flow rates at which the thermal diffusion already plays an important role.

The data of Britzke and Kapustinsky are in best agreement with those of the present work. They were obtained by a static method of measuring the partial pressure of hydrogen in the hot zone by letting it diffuse through the walls of a platinum bulb. However, some uncertainty must exist in this method too; their data show a minimum for the gas ratio at 957°C, although no break in the curve is to be expected at this temperature from the equilibrium diagram.

THE EQUILIBRIUM DIAGRAM OF THE SYSTEM

The experimental data confirm previous data that a region of liquid immiscibility exists in the system. At the monotectic temperature of about 900°C,* the silver-rich phase has a composition of 5.5 at. pct sulphur (corresponding to run 5) and the sulphur rich phase about 31.0 at. pct. This agrees with the compositions obtained from thermal analysis by Kracek: 5.8 and 31.1 at. pct sulphur.[10] At higher temperatures, the immiscibility gap becomes narrower and disappears at a critical temperature of about 1125°C (±25°C) and a critical composition of 24 at. pct sulphur. This corresponds to a rather unsymmetrical shape of the immiscibility region. The immiscibility region and the neighboring parts of the equilibrium diagram are shown in Fig 7.

The present investigation gives little information as to the solid solubility of sulphur in silver. Run 9 shows that the solid solubility at 800°C is not greater than 0.50 at. pct (0.15 wt pct) sulphur. The actual solid solubility is probably much less.

Thermodynamic Calculations

Thermodynamic calculations will be carried out separately for the different regions of the system.

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* Kracek[10] found the monotectic temperature equals 906°C. The present work indicates a temperature of 895–900°C. However, the temperature reading in this work may be a few degrees off, and it is further probable that hydrogen dissolved in the liquid metal will lower the freezing point another couple of degrees. Therefore, the value of Kracek is regarded as most reliable.

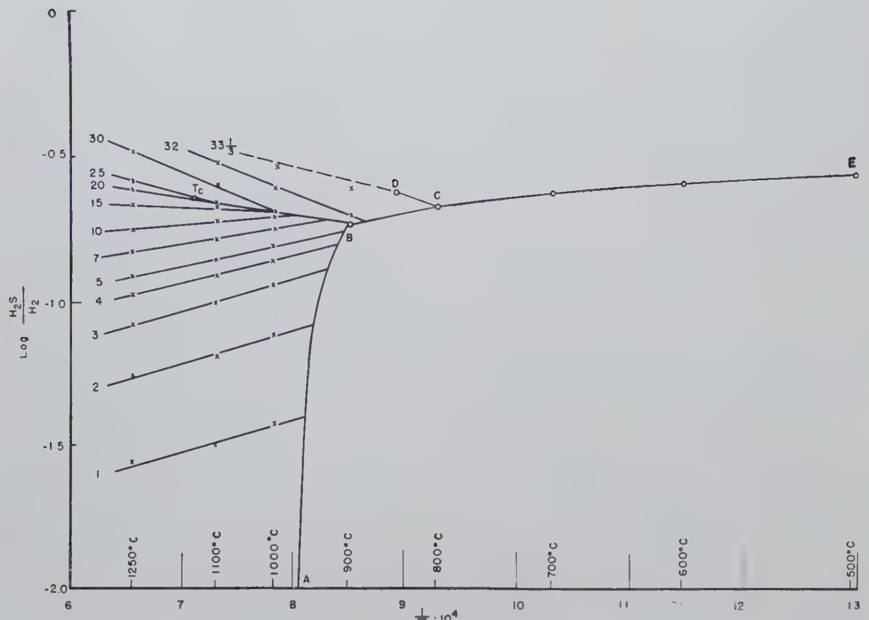

FIG 5—Log H_2S/H_2 as a function of $1/T$.
Figures to the left give sulphur content of the alloy in atomic per cent.

1. Below 800°C, the investigated equilibrium corresponds to the reaction:

$$Ag_2S_{(solid)} + H_{2(gas)} \rightarrow 2Ag_{(solid)} + H_2S_{(gas)}$$

The equilibrium gas ratio is independent of the relative amounts of the two solid phases, as long as they are both present.

The mean values of the equilibrium constant, averages of five runs, are listed in Table 2 for four different temperatures.

The standard Gibb's free energy $\Delta F°$ for the reaction is derived by the expression $\Delta F° = -RTlnKp$

The slope of log Kp plotted against $1/T$ as done in Fig 5, gives us the heat of the reaction:

$$\Delta H = \frac{-RdlnKp}{1/T}$$

Furthermore:

$$\left[\frac{d\Delta H}{dT}\right]_P = \Delta Cp$$

where ΔCp is the increase in specific heat resulting from the reaction.

In the following, a calculation will be carried out to derive expressions for the heat and Gibb's free energy of the reaction, as a function of temperature, on the basis of the experimental data and the specific heats of the components involved. The procedure for these calculations is the same as that used by Watanabe, except that more recent data are applied for the specific heats. For the specific heats Cp, the values listed by Spencer,[11] for the gases, and by Kelley,[12] for the solids, are used.

Silver sulphide exists, according to Kracek,[10] in three modifications denoted III (below 176°C), II (176–586°C), and I (586-mp). The heat of transformation at 176°C = 449°K is given by Kelley.

$$Ag_2S_{III} \rightarrow Ag_2S_{II}$$
$$\Delta H_{449} = 1000 \text{ cal/mol}$$

The heat of transformation $Ag_2S_{II} \rightarrow Ag_2S_I$ is not known. Kracek finds that the heat effect at 586°C is less than one-tenth of the heat effect at 176°C. This indicates that the heat of the reaction $Ag_2S_{II} \rightarrow Ag_2S_I$ is less than 100 cal which is inside the experimental error of the present work.

Likewise no data exist on the specific heat of Ag_2S_I. It cannot, however, be much different from that of Ag_2S_{II}, and no appreciable error will be introduced by using this value above 586°C also.

Thus, the transformation at 586°C is entirely disregarded in the present calculations.

For the reaction:

$$Ag_2S_{I\text{ and }II} + H_2 \rightarrow 2Ag + H_2S$$
$$\Delta Cp = -9.683 + 7.052 \cdot 10^{-3}T + 0.304 \cdot 10^{-6}T^2 - 0.634 \cdot 10^{-9}T^3$$

and

$$\Delta H = 4720 - 9.683T + 3.526 \cdot 10^{-3}T^2 + 1.01 \cdot 10^{-6}T^3 - 0.159 \cdot 10^{-9}T^4 \quad [1]$$
$$\Delta F° = 4720 + 22.29T \log T - 3.526 \cdot 10^{-3}T^2 - 0.051 \cdot 10^{-6}T^3 + 0.053 \cdot 10^{-9}T^4 - 65.11T \quad [2]$$

From the last expression, $\Delta F°$ and log Kp are calculated for comparison with the experimental data. They are listed in the last columns in Table 2. The agreement is satisfactory.

If the expressions 1 and 2 are combined with corresponding expressions for the reaction $H_2S \rightarrow H_2 + \frac{1}{2}S_2$, one obtains the heat and free energy for the reaction $Ag_2S \rightarrow 2Ag + \frac{1}{2}S_{2(gas)}$; and one can also derive the partial pressure of S_2 vapor. These calculations will not be done here.

Table 2 . . . Mean Values of Equilibrium Constant

$Ag_2S_{(s)} + H_{2(g)} \rightleftarrows 2Ag_{(s)} + H_2S_{(g)} \qquad Kp = \frac{H_2S}{H_2}$

t°C	T°K	Kp exp.	Kp calc.	ΔF° exp.	ΔF° calc.
500	773	0.263	0.264	2050 cal	2043 cal
600	873	0.249	0.248	2414 cal	2418 cal
700	973	0.232	0.231	2830 cal	2836 cal
800	1073	0.215	0.214	3281 cal	3289 cal

On the basis of Eq 1 and 2, the values for the heat and free energy at the transformation temperature 449°K are obtained.

For the reaction $Ag_2S_{II} + H_2 \rightarrow 2Ag + H_2S$

$$\Delta H_{449} = 1084 \text{ cal and } \Delta F°_{449} = 1316 \text{ cal}$$

and for the reaction $Ag_2S_{III} + H_2 \rightarrow 2Ag + H_2S$

$$\Delta H_{449} = 1084 + 1000 = 2084 \text{ cal}$$
$$\Delta F°_{449} = 1316 \text{ cal}$$

Below 449°K, one has:

$$Ag_2S_{III} + H_2 \rightarrow 2Ag + H_2S$$
$$\Delta H = 4370 - 6.683\,T + 3.526{\cdot}10^{-3}T^2 + 0.101{\cdot}10^{-6}T^3 - 0.159{\cdot}10^{-9}T^4 \quad [3]$$
$$\Delta F° = 4370 + 15.39\,T \log T - 3.526{\cdot}10^{-3}T^2 - 0.051{\cdot}10^{-6}T^3 + 0.053{\cdot}10^{-9}T^4 + 46.01T \quad [4]$$

This gives for 298°K = 25°C

$$\Delta H_{298} = 2693 \text{ cal} \quad \Delta F°_{298} = 1692 \text{ cal}$$

The heat and free energy of the reaction $H_2S = H_2 + S_{rh}$ at 298°K are known[1]

$$\Delta H_{298} = 4800 \text{ cal} \quad \Delta F°_{298} = 7865 \text{ cal}$$

Combining these two sets of values, one obtains for the formation of 1 mol of silver sulphide from the elements at room temperature:

$$2Ag + S_{rh} = Ag_2S_{III}$$
$$\Delta H_{298} = -7493 \text{ cal}$$
$$\Delta F°_{298} = -9557 \text{ cal}$$

The largest uncertainties in the present calculation are in specific heats of the silver-sulphides which are known with an accuracy of only 5 pct, which causes an uncertainty of 600 cal in the calculation of the heat and free energy at room temperature. The determination of the heat of reaction at high temperature is probably correct to ±200 cal; hence the total uncertainty in ΔH_{298} and $\Delta F°_{298}$ will be 800 cal.

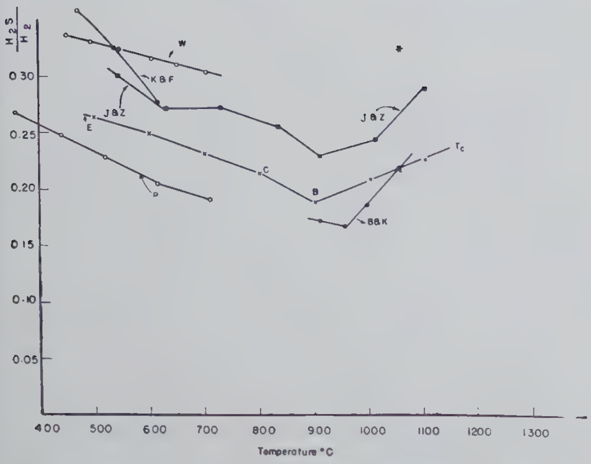

FIG 6—Comparison of present results with results of previous investigators.

P = Pelabon
K & F = Keyes and Felsing
J & Z = Jellinek and Zakowski
ECBTC = Result of the present work
W = Watanabe
B & K = Britzke and Kapustinsky
* = Gas ratio for run without circulation allowing thermal diffusion to take place

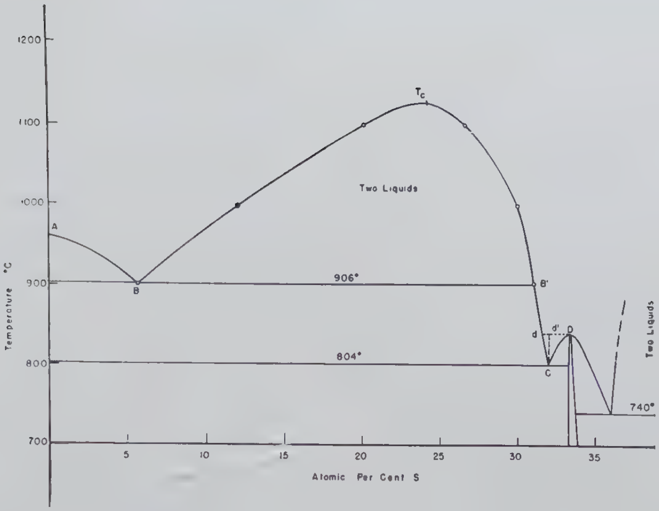

FIG 7—Phase diagram for the melting region of the system silver/silver-sulphide.

The heat of formation of Ag_2S from the elements has been determined experimentally by Zeumer and Roth[13] to $\Delta H_{293} = -6{,}660 \pm 200$ cal.

The standard free energy of formation is listed by Latimer[14] as $-9{,}500$ cal, a value with which the present result is in very good agreement. Latimer's value is the average of independent measurements of equilibrium constants in aqueous solutions.

The standard free energy has also been given by Kelley as $-8{,}680$ cal, but his value is based on the equilibrium constants at high temperature by Keyes and Felsing, Jellinek and Zakowski, and Watanabe in combination with the heat of reaction adapted from Zeumer and Roth.

THERMODYNAMIC RELATIONS IN THE MOLTEN STATE

Calculations of the heats of reaction and free energies for the *heterogeneous* reactions above the melting point, for instance Ag_2S-rich melt + $H_2 \rightarrow$ Ag-rich melt + H_2S, can be done in the same way as for the solid equilibrium. Such calculations have rather little physical significance as they involve phases in which the composition changes considerably with the temperature.

A clearer description of the thermodynamics in the molten state is obtained by plotting the partial thermodynamic functions for sulphur and silver as a function of the composition. The partial atomic heat content of sulphur dissolved in the melt can be expressed in different ways, depending on what standard state is chosen:

The heat of the reaction $H_2S \rightarrow H_2 + S_{(\text{dissolved})}$ will be denoted by $\Delta\bar{H}_S$ and is the heat required to transfer one gram atom of sulphur from hydrogen sulphide to the melt—the melt being kept at constant composition.* $\Delta\bar{H}_S$ is given by the expression

$$\Delta\bar{H}_S = R\frac{dl_n H_2S/H_2}{dl/T}$$

and can be obtained from the slope of the curves in Fig 5.

If, on the other hand, the partial heat content of sulphur is referred to monoatomic sulphur vapor as the standard state, it will be denoted by $\Delta\bar{H}_S'$. In the temperature region 1000–1250°C $\Delta\bar{H}_S$ and $\Delta\bar{H}_S'$ will differ by 74.680 cal which is the heat of the reaction $H_2S \rightarrow H_2 + S_{(g)}$ in this temperature range, calculated from Kelley's data.[1]

The partial heat content of silver, $\Delta\bar{H}_{Ag}$, is related to the corresponding value for sulphur by the equation

$$N_{Ag}\, d\Delta\, \bar{H}_{Ag} + N_S d\, \Delta\bar{H}_S = 0$$

N_{Ag} and N_S mean the atomic fractions of silver and sulphur respectively. This equation is independent of what standard state is chosen for sulphur. Integrating this equation graphically, the partial heat content of silver referred to pure molten silver as standard state, can be derived. The partial heats $\Delta\bar{H}_S$, $\Delta\bar{H}_S'$ and $\Delta\bar{H}_{Ag}$ are plotted in Fig 8, all as a function of composition.

A few points became apparent from Fig 8; the partial atomic heat of sulphur is independent of concentration in the dilute range 0–3 at. pct sulphur, that is, Henry's law is followed.

Between 3 and 30 at. pct sulphur, the partial heat of sulphur $\Delta\bar{H}_S$ decreases linearly with the sulphur content. Between 30 and 33⅓ at. pct sulphur, the atomic heat seems to increase somewhat. The experimental data are not too good here, however, and a considerable error is possible.

Contrary to what is usually the case for a solute, the partial heat of sulphur decreases with increasing concentration. In a later section this phenomenon will be more thoroughly discussed, as well as its relation to the immiscibility phenomen in this system.

The chemical potential μ_S and the chemical activity a_S of sulphur in the melt are given by the equations

$$\mu_S = RT \ln H_2S/H_2 + \mu_S{}^0$$
$$a_S = K_1 \cdot H_2S/H_2$$

The standard potential $\mu_S{}^0$ and the constant K_1 depend again on what standard state is chosen for sulphur.

Using the Gibbs-Duhem equation, we can derive the chemical activity of silver a_{Ag}:

$$N_{Ag}\, dln\, a_{Ag} + N_S\, dln\, H_2S/H_2 = 0$$

This equation is integrated graphically and pure molten silver is given the activity one.

The chemical activity of Ag_2S is defined by the expression

$$a_{Ag_2S} = K_2(a_{Ag})^2 \cdot H_2S/H_2$$

The constant K_2 is so chosen as to make a_{Ag_2S} unity at the stoichiometric composition.

In Fig 9, the chemical activity of silver, the H_2S/H_2 ratio and the chemical activity of Ag_2S are plotted for the temperature 1125°C (the critical temperature of immiscibility).

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* $\Delta\bar{H}_S$ is independent of the partial pressure of H_2S, which behaves as a perfect gas.

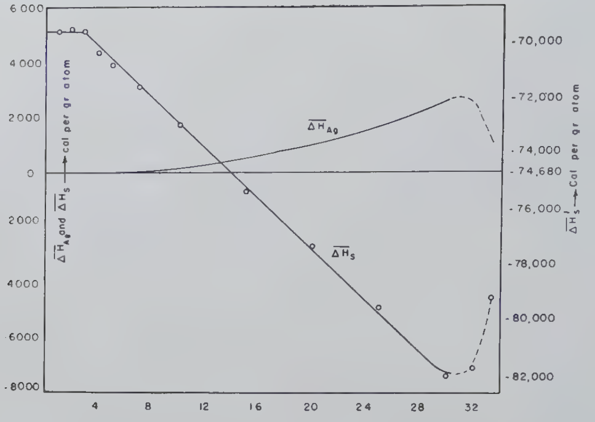

FIG 8—Partial atomic heat content of silver and sulphur.
Figures along the abscissa indicate atomic pct sulphur.
$\Delta\overline{H}_S$ and $\Delta\overline{H}_{Ag}$ are read on the scale to the left.
$\Delta\overline{H}_{S'}$ is read on the scale to the right.

The typical positive deviation from Raoult's law is apparent for all three curves, and they all have a horizontal tangent at 24 at. pct sulphur, corresponding to the critical composition.

One can further see that the activity of silver has a considerable value even for a melt of composition Ag_2S. Thus, the system Ag-Ag_2S cannot be treated thermodynamically as a simple binary system but only as part of the system Ag-S.

The activity of silver follows Raoult's law in the silver rich part of the system —the activity of sulphur following Henry's law.

THE HEAT OF FUSION OF Ag_2S

The heat of fusion of Ag_2S may be determined in two different ways:

1. The break in the curve ECB (Fig 5) at the eutectic temperature 804°C corresponds to about 900 cal. This would be equal to the heat of fusion if there were no change in the partial heat content and partial free energy of molten Ag_2S between 31 and 33⅓ at. pct sulphur. Because this assumption is not strictly correct, the actual heat of fusion will be somewhat less than 900 cal.

2. Knowing the variation of the activity of Ag_2S in the melt between 31 and 33⅓ at. pct sulphur, and the lowering of the freezing point of Ag_2S by addition of silver, the heat of fusion can be determined by the equation

$$\frac{dT_m}{dx} = \frac{RT^2}{\Delta H_m}\left(\frac{\partial \ln a_{Ag_2S}}{dx}\right)_T$$

x = atomic fraction of silver
T_m = freezing temperatures
ΔH_m = heat of fusion of Ag_2S

The chemical activity of Ag_2S is proportional to the product $(a_{Ag})^2$. H_2S/H_2; the freezing point lowering is obtained from the work of Kracek,[10] and a value for ΔH_m of about 700 cal is obtained.

This method involves a considerable degree of uncertainty and the obtained value must be regarded as preliminary.

It seems likely, however, that the heat of fusion is considerably lower than the 3400 cal per mol listed by Kelley.[15] The disagreement is so large that a redetermination by more accurate methods is desirable.

A value for the heat of fusion of 700–900 cal is amazingly low and would correspond to an entropy of fusion of less than one calorie per degree per mol. Very few substances are known to have an entropy of fusion that low (a value from 2–5 units per mol is usual). On the other hand, a very low entropy of fusion is to be expected from the crystal structure of solid Ag_2S which according to Rahlfs[16] shows a high degree of disorder. In this crystal structure the silver atoms are almost randomly distributed and can be compared with the atoms in a liquid, whereas only the sulphur atoms form a regular lattice. Therefore, the entropy of fusion should correspond to the breaking down of the sulphur lattice only.

A Tentative Theory for the Relation between Thermodynamics and Structure of the Melt

Little is known about the structure of molten metals and alloys and especially meager is our knowledge of the structure and chemical forces in molten metal-sulphur systems. For the following treatment, a few known facts will be summarized:

1. Solid silver crystallizes in a close packed cubic structure with coordination number 12 and distance between nearest neighbors = 2.88Å.

2. Molten silver has a structure closely related to that of solid silver but lacks the long range regularity of the solid state. The coordination number is 11–12 and nearest neighbor distance slightly more than in the solid. In the following, an average coordination number of 11.5 will be assumed. In both solid and liquid silver, the interatomic bond is metallic.

3. Solid Ag_2S (modification II) crystallizes in a cubic structure, where the silver atoms are almost randomly distributed (per unit cell 4 silver atoms can occupy 42 positions).[16] Each sulphur atom has about seven nearest silver neighbors at a distance of about 2.6Å. The distance to the nearest eight sulphur atoms is 4.225Å. Each silver atom has on the average about ten nearest silver neighbors at a distance of about 3.0Å. The crystal structures of modifications I and III are not known in detail but are regarded as closely related to modification II. Therefore, the number of nearest neighbors and the distance between them should be about the same as in modification II. As the heat of fusion of Ag_2S seems to be very low, the structure of the melt should not be expected to differ very much from the solid state.

The nature of the interatomic bond in Ag_2S can be described as predominantly metallic since the compound exhibits electronic conductivity with a negative temperature coefficient.[17] There is no reason to assume the nature of the interatomic bond to be any different in the liquid than in the solid state.

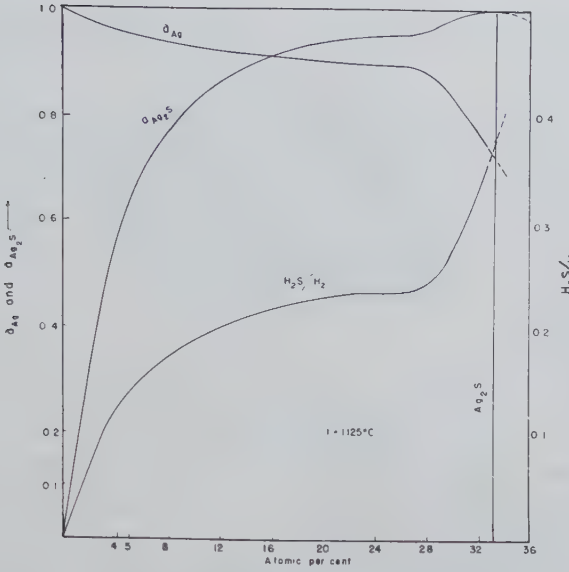

FIG 9—Chemical activities for silver and silver sulphide and the ratio H_2S/H_2 at $t = 1125°C$.
The gas ratio is a measure of the chemical activity of sulphur.

One should, therefore, in this compound apply the atomic radii for metallically bonded atoms rather than the ionic radii. The atomic radii which are in best harmony with the interatomic distances are 1.5Å for silver and 1.1Å for sulphur.

The ratio R_S/R_{Ag} is close to 0.73. For a close packing of atoms, this would correspond to a coordination number: 8 (silver neighbors around each sulphur atom) while 7 is actually found in solid Ag_2S. For the discussion of the structure of the melt, the average coordination number is assumed equal 7.5.

We will discuss the energy required to introduce one gram-atom of sulphur from monatomic vapor into molten silver or into a silver-sulphur melt, the melt being kept at constant temperature. This energy equals $\Delta\overline{H}_S'$ from the preceding section. It will be necessary to expand one of the interstitial positions in the silver melt to make room for each sulphur atom. Structural consideration indicates that this requires the breaking an average of 1.5 Ag-Ag bonds, and a slight adjustment of the silver atoms. If more and more sulphur atoms are added to the melt, more interstitial positions are expanded, each requiring the breaking of 1.5 Ag-Ag bond. When one gram atom sulphur has been added to 2 g atoms silver corresponding to a composition Ag_2S, 1.5 N out of 11.5 N Ag-Ag bonds have been broken, leaving 10 N bonds unbroken, corresponding to each silver atom being surrounded by 10 silver neighbors. This agrees with the coordination number 10 which is actually found in solid Ag_2S.

The energy required to introduce one gram atom of sulphur from monatomic vapor into the melt will be the energy required to break N 1.5 Ag-Ag bond minus the energy liberated by the formation of new interatomic bonds. The energies of the interatomic bonds will be denoted by the symbol V.

For a diluted solution of sulphur in molten silver, the individual sulphur atoms will be sufficiently separated not to interact and

$$\Delta\overline{H}_S' = N\cdot(1.5V_{Ag\text{-}Ag} - 7.5\ V_{Ag\text{-}S})$$

As $\Delta\overline{H}_S'$ according to Fig 8 equals −69,500 cal for a dilute solution, and $N\cdot V_{Ag\text{-}Ag}$ is calculated from the heat of vaporization of liquid silver equal 12,000 cal, one obtains the energy of N silver-sulphur bonds, $N\cdot V_{Ag-S}$, equal 11,650 cal.

With increasing sulphur concentration, we find that $\Delta\overline{H}_S'$ decreases and reaches a value of about −82,000 cal when the composition approaches Ag_2S.

This decrease in heat content is very likely due to the fact that more and more sulphur atoms will occupy neighboring "expanded interstitial" positions, that is, they will be second nearest neighbors in the melt, and that these sulphur neighbors exhibit attractive forces on each other. Thus, bringing two sulphur atoms into neighboring "interstitial" positions will liberate a certain energy $V_{S\text{-}S}$.

The fact that the energy of the sulphur-sulphur bond has a positive value means that each sulphur atom will tend to attract other sulphur atoms to have as large a number of sulphur neighbors as possible. On the other hand, thermal agitation will tend to distribute the sulphur atoms statistically among the available positions to make the entropy as large as possible. The net effect is a distribution of the atoms which gives the lowest free energy. The number of sulphur neighbors in neighboring "interstitial" positions will be somewhat larger than corresponds to random distribution. We will have a type of short range order in the melt. (See Fig 10.)

The total free energy of mixing can, for a given temperature, be expressed in the following terms:

$$\Delta F(x, n) = \Delta H(x, n) - T\Delta S(x, n)$$

x is the mol fraction of sulphur and n the number of sulphur-sulphur bonds. ΔH will decrease with increasing value of n, and ΔS will decrease with increasing value of n in excess of what corresponds to random distribution.

If the exact dependencies of ΔH and ΔS with respect to n were known, the minimum value of ΔF and the degree of short range order could be obtained by setting

$$\left(\frac{\partial \Delta F}{\partial n}\right)_x = 0$$

Such a statistical derivation, especially of the entropy, cannot at the present be carried out.

The energy of the sulphur-sulphur bond can be derived from the difference in $\Delta\overline{H}_S$ for a stoichiometric and a diluted melt. This difference is 12,500 cal. On the assumption that each sulphur atom has 8 sulphur neighbors in a melt of stoichiometric composition, as it has in solid Ag_2S, the energy of N sulphur-sulphur bonds will be: $N\cdot V_{S\text{-}S} = 1560$ cal.

The energy of the interatomic bonds will not vary much with temperature. By decreasing temperature however, the term $T\Delta S$ in the free energy expression will decrease, allowing an increase in the degree of short range order. But an increase in short range order of this kind cannot go on indefinitely with maintenance of the homogeneity of the melt. The sulphur atoms will more and more accumulate into clusters separated from each other by regions where concentration of sulphur atoms is small. When the cluster formation has reached a certain extent, large enough to overcome the surface tension, the melt will break down into two liquids, one rich in sulphur corresponding to the Ag_2S-rich phase and one low in sulphur corresponding to the Ag-rich phase.

Thus there is a close relationship between the decrease in $\Delta \overline{H}_S$ with increasing sulphur concentration, the degree of short range order in the melt, and the fact that it separates into two layers by cooling.

The author is aware of the fact that this last section has been rather speculative and suffers from errors of oversimplification. Thus, for example, it is not strictly correct to assume the size of the atoms, and consequently the coordination number, to be absolutely constant all through the system. The assumption that the energy of the individual interatomic bonds are independent of the composition is also probably incorrect. But the errors thus introduced will be small compared with the large variation of $\Delta \overline{H}_S$ going from diluted to stoichiometric composition.

The main idea has been to introduce a general concept of the structure of a metal/sulphur melt and show that such a concept is consistent with observed thermodynamic properties. It is unlikely that the atomic arrangement in other metal/sulphur systems is in principle different from that of the system silver/sulphur. Most metal/sulphur systems show either immiscibility between a metal melt and a sulphide melt, or miscibility with a pronounced positive deviation from Raoult's law. Also in these cases, short range order should exist in the melt, although there is no reason to assume the existence of defined sulphide molecules. It follows therefore, that the discussion of which sulphides do exist, for example, in molten steel (a discussion which is common among metallurgists) is somewhat beside the point. One should rather discuss the influence of different alloying elements on the chemical activity of dissolved sulphur, and on the interatomic arrangement.

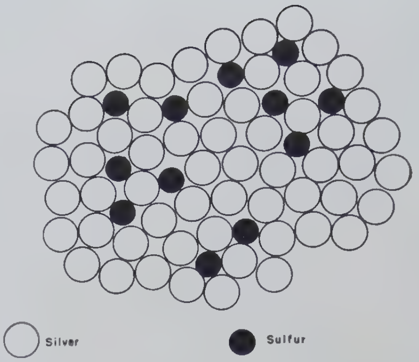

FIG 10—Two dimensional sketch of the suggested atomic arrangement for a silver-sulphur melt containing about 20 at. pct sulphur, indicating short range ordering of the sulphur atoms.

The author hopes, in another paper, to return to this last subject.

Summary

A thermodynamic investigation of the system silver-silver sulphide has been undertaken. The principle of this investigation is the reaction of sulphur from the silver sulphur alloys with hydrogen to form hydrogen sulphide, the equilibrium ratio H_2S/H_2 being a measure of the escaping tendency of sulphur.

An apparatus was designed in which the equilibrium gas ratio was obtained by circulating the gas mixture over the specimen, and the composition of the gas mixture was subsequently determined from its density by means of a buoyancy-balance (see Fig 1). The possible sources of error were discussed.

Altogether, 22 samples containing up to 33.3 at. pct sulphur have been studied over the temperature range 500–1300°C. The equilibrium ratios H_2S/H_2 are plotted as a function of temperature in Fig 3 and 5 and as a function of alloy composition in Fig 4.

It was shown that the immiscibility region in the system has a critical temperature of about 1125°C corresponding to a critical composition of 24 at. pct sulphur (see Fig 7).

The heat and standard free energy of the reaction $Ag_2S_{(s)} + H_{2(g)} \rightarrow 2Ag_{(s)} + H_2S_{(g)}$ were obtained from the experimental data and are expressed as functions of temperature.

The heat and standard free energy of formation of Ag_2S from the elements have been calculated for room temperature,

$$\Delta H_{298} = -7493 \text{ cal and } \Delta F^{\circ}_{298} = -9557 \text{ cal}$$

The heat of fusion of Ag_2S has been estimated to 700–900 cal.

The partial heat content and chemical activity of sulphur in the liquid phase have been computed and the corresponding values for silver have been calculated by means of the Gibbs-Duhem equation (see Fig 8 and 9).

The last section contains a discussion of the relation between thermodynamics and the structure of the silver-silver sulphide melts. A model of the structure is suggested, the model being consistent with observed thermodynamic data and also with the existence of immiscibility in the system. (See Fig 10.)

Acknowledgment

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Autogenous Roasting of Low Grade Zinc Concentrate in Multiple Hearth Furnaces at Risdon, Tasmania

J. A. B. FORSTER*

The operations of the Electrolytic Zinc Co. of Australasia Ltd. involve the preliminary roasting of zinc concentrate from Broken Hill, New South Wales, at a number of acid-making centers on the Australian mainland. The partially roasted material is shipped to the Tasmanian plant where it was formerly re-roasted prior to leaching,[1] but this practice was gradually abandoned in favor of the flotation of leach residue for the recovery of a concentrate containing about 22 pct sulphide sulphur and known as secondary or Risdon concentrate.[2] This change, together with increased zinc production, called for new furnaces at Risdon for the roasting of 40–50 tons† of secondary concentrate and 90 tons of new concentrate per day.

The war situation made it imperative that construction be commenced without delay and to save time it was decided to base the design on that of Skinner type furnaces which had been built in South Australia twenty years earlier.

This involved some sacrifice of desirable features but did not prevent the incorporation of provisions which had enabled small Herreshoff type furnaces to roast secondary concentrate autogenously. The roasting rate in existing furnaces was 10–12 lb sulphide sulphur per sq ft of hearth area per day, and eleven hearths, 20 ft in diam, were provided in the two new furnaces in anticipation that they would prove capable of the autogenous roasting of 130–140 tons of concentrate per day from 28–29 pct sulphur down to 4.5–5 pct, with an oxidation rate of 11–11.5 lb S/S per sq ft of hearth area per day.

It was soon realized, when the first of the furnaces went into operation, that a much better performance than this might be given, and the purpose of this paper is to show how a treatment rate of 100 tons per furnace day, and oxidation rates approaching 15 lb S/S per sq ft per day have been reached.

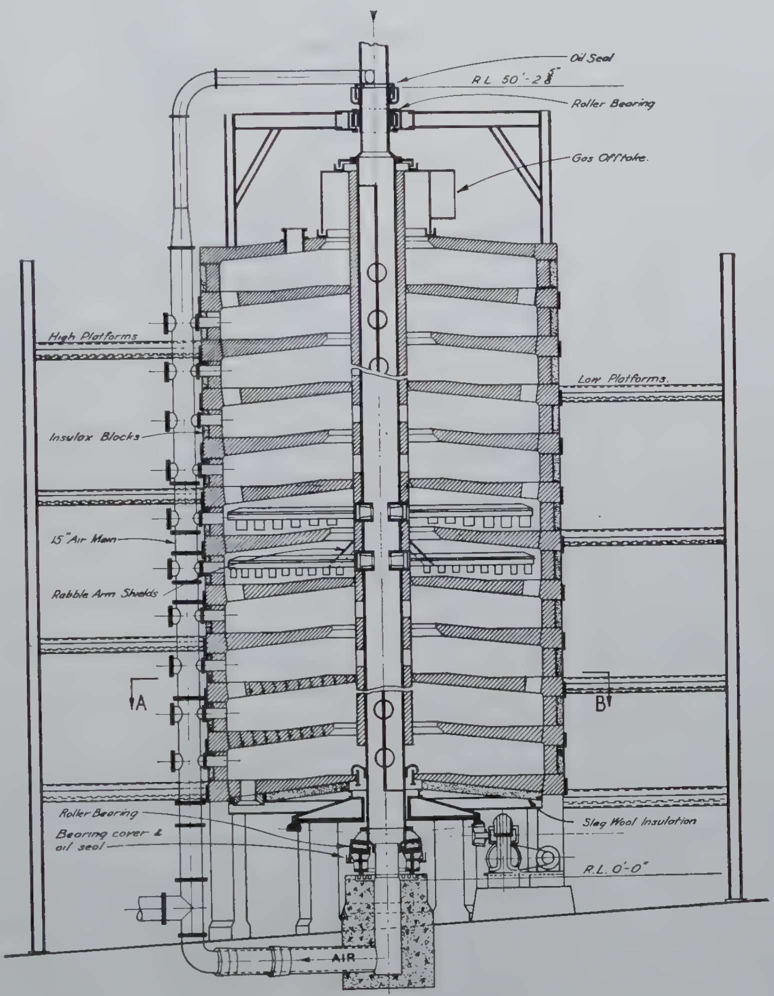

FIG 1—Composite section.

Furnace Design

General specifications for the design were based on the results of experience with several other types of furnace and on the special operating conditions

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* Superintendent, Roasting and Casting Division, Risdon Works, Electrolytic Zinc Co. of Australasia, Ltd., Tasmania.

† Throughout this paper the ton is 2240 lb.

[1] References are at the end of the paper.

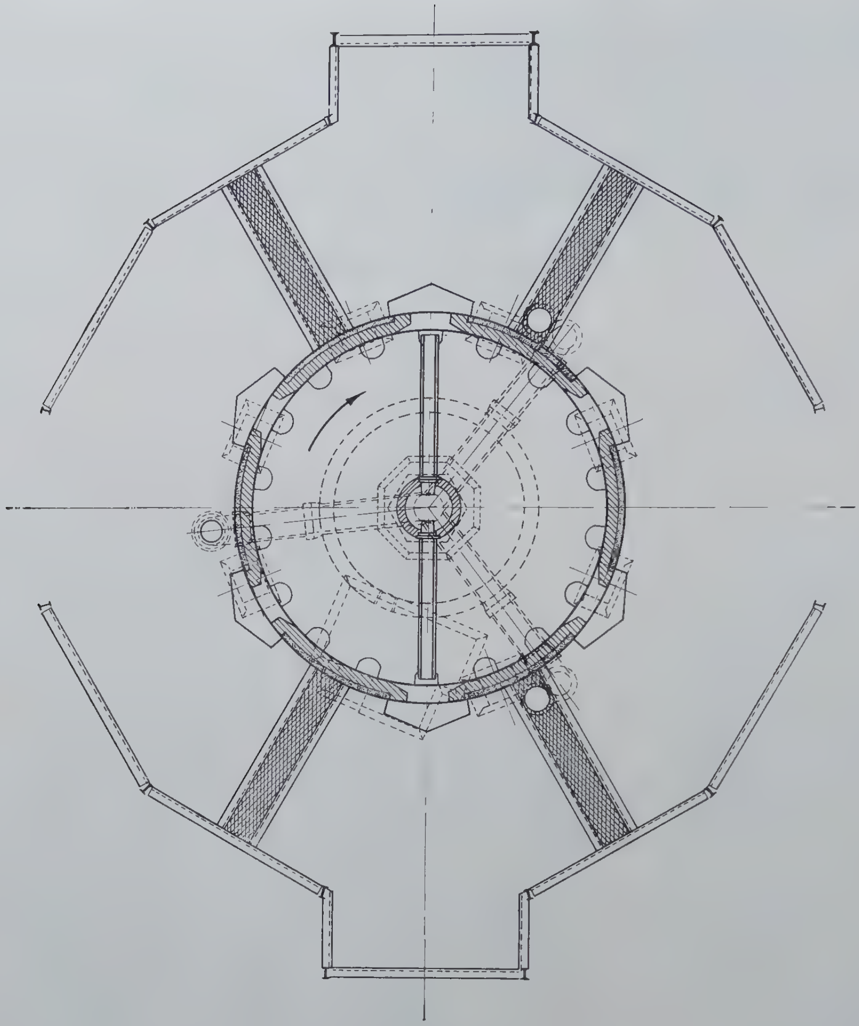

FIG 2—Plan A-B (See Fig 1).

expected. The general arrangement is shown in Fig 1, 2 and 3.

The original hearths had a camber of 8 in. and were very difficult to keep clean. To build flat hearths involved major changes in design, and a compromise was reached by thickening the haunch blocks and five outer rings of hearth blocks as much as minimum door size would allow, but the original camber remains in the central portions of the hearths.

The working doors are covered by outer doors which form chutes right down the face of the furnace to hoppers in the basement where spillage and cake from the hearths are collected. These chutes are ventilated by a fan which exhausts from both top and bottom of each chute so as to be effective when any door is open.

The column and rabble arms are air cooled, and the air leaving the bottom of the column is distributed to three mains rising alongside the furnace. Air is supplied to the hearths from these mains through ports controlled by disc valves. The tops of the mains are connected through a damper to the fan supplying the rabble-cooling air. This arrangement permits hot air to be supplied to all hearths when necessary, while cold air may be used down to any desired level of the furnace. Hot air may be exhausted to atmosphere when desired.

In the second furnace, Nos. 6, 7, and 8 hearths are each provided with an additional port for the injection of dust recovered from the furnace gases by means of cyclones. An additional port in No. 9 hearth accommodates a small oil burner which is not in continuous use.

Rabble arms are of cast iron and have an indefinite life. The rabble teeth in No. 1 hearth are of special cast iron and last 2–3 years; all other teeth are 27 pct Cr and the average life is 3½ years.

Design and Arrangement of Rabble Teeth

A large contribution to the present performance of these furnaces has been made by improvement in the design and arrangement of rabble teeth. There are five factors of importance in design: angle of approach, throw, spacing, depth and overlap. These have not always had the attention they deserve, though this may mean the difference between failure and success of a furnace.

Angle of approach is the angle between the blade of the tooth and the tangent to its circle of movement. If this angle is too large the material being rabbled will not slip across the blade but will tend to build up in front and to be pushed around the furnace; an overloaded condition will quickly develop. If the angle is smaller than need be the blade of the tooth will be too long and heavy in relation to the work required of it. The smaller the angle and the longer the tooth the more difficult it will be to clean the blades when necessary. The angle may be relatively large for material moving down a slope or outward across the hearth, but must be smaller for the same material on upward slopes and for inward rabbling. Free moving material like dry sand can be worked with the most economical angle, 45°, on outward traverses, but angles of less than 30° may be necessary for sluggish or "sticky" material on inward traverses.

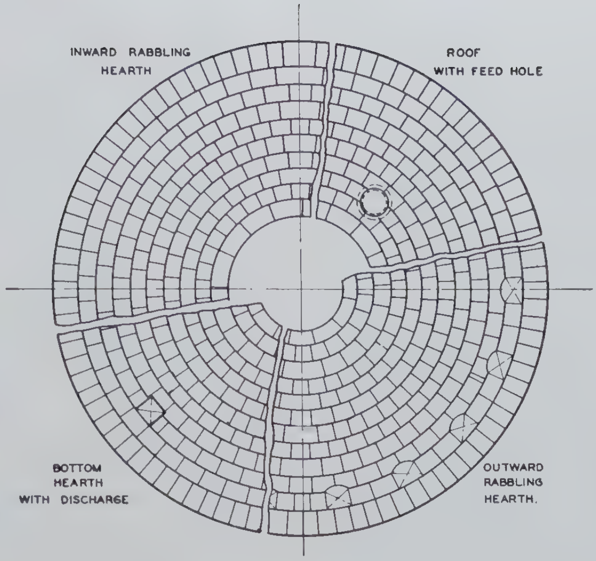

FIG 3—Composite hearth plan.

The throw is the radial distance between the leading and trailing edges of the teeth; it is rather more than the effective radial distance of the movement of material because of "slip"—that is, the material which, as the trailing edge passes on, slips back from the rill of the tooth into its path. In the first place the throw determines the number of times the roasting material will be turned over during its traverse of the hearth; consequently it has an important bearing on the amount of roasting done on the hearth. Long throw thins the mobile bed and may be a factor in overcoming an overloading tendency. Throw also determines, to some extent, the spacing of the teeth, and hence the convenience with which tooth cleaning is done, and its frequency.

Spacing, the center to center distance of the teeth on the arm, must not be too small or the cleaning of teeth becomes a difficult operation likely to result in mishap. Under heavy loads close spacing also means increased friction in the passage of material between teeth and makes the development of overloading more probable, besides decreasing the exposure of the material to the furnace atmosphere. In determining spacing, allowance must be made for any tendency of the material to crust on the teeth as this of course decreases the effective spacing between successive cleanings. Spacing must not exceed the throw multiplied by the number of arms in the hearth if the whole of the hearth is to be swept by the teeth, but if the material rills easily and a deep mobile bed is desired, it is possible even to double this figure and have considerable bands of unswept hearth, particularly if the throw is relatively small.

The depth of the teeth determines firstly the depth of immobile bed on the hearth, and secondly, in conjunction with spacing, the maximum cross section of material which can be moved effectively at each pass of the arm. Where the material has to traverse a slope it is the depth of tooth nearest the crest which is the determining or effective depth of all teeth on the hearth. If the effective depth of tooth divided by the spacing is less than the tangent of the angle of rest of the material, the furnace will be unable to attain its possible transport capacity, but it is not of much advantage for this value to be exceeded greatly unless a deep, slow-moving bed is to be maintained by having the spacing exceed the throw multiplied by the number of arms, or unless two teeth of opposite throw are used together to form a "scoop" for gathering material into a drophole.

On a flat hearth "slip" is normally a little less than one-eighth of the mobile load gathered by the tooth; on downward slopes and outward traverses it is less, on upward slopes and inward traverses it is more. On cambered inward rabbling hearths, the greater slip tends to increase slip still further, so that there is a distinct tendency for such hearths to become overloaded and, finally, completely choked. It is important in such cases to keep the upward slope to a minimum by having as little immobile bed as possible near the crest. A further and effective remedy is the use of some overlap, that is, having the paths of teeth on one arm overlap the paths of those on the preceding and following arms. It is present when spacing is less than throw multiplied by the number of arms; (by 2 in the special case where four arms operate as two effective pairs). This is, of course, a particular case of the general principle that increased throw tends to thin the mobile bed, for the simplest way of getting overlap is to increase the throw of the teeth without altering the spacing.

Where two teeth of opposite throw are used to form a V or scoop for gathering large quantities of material, as in the case of a final hearth where the whole load has to be concentrated to a single drophole, it is essential that the base of the scoop be sufficiently open to leave a considerable trail of material behind it. The ideal opening will permit so much to escape that the scoop will have accumulated its full load only shortly before it reaches the drophole. In the final hearth it is also desirable, if the load is large, that each arm should carry a scoop commanding the drophole, but these scoops should not work over identical paths.

A significant factor in all rabbling is that on outward rabbling hearths the load is being spread over a larger and larger area, as it progresses, while the reverse is the case on inward rabbling hearths. To secure the best possible combination of roasting and transport capacities the throw of teeth should be at the practical minimum at the outer ends of the arms and increase progressively inwards. This calls for a great diversity of patterns, and, except for the use of some overlap, has not been adopted in the Risdon furnaces, mainly because roasting capacity has already reached a level which makes gas velocity through the third hearth dropholes as high as is desirable; the use of shorter throw teeth in the outer parts of the lower hearths is contemplated as a means of still further improving the completeness of the roast.

Within a few weeks of starting, the first furnace was being operated to the full capacity of its hearth transport system, which proved, under test, to be about 75 tons per day, nonstop. It was obvious that the furnace had by no means attained its full roasting capacity, and if this were to be realised an increase of transport capacity must be obtained. In fact, a very big increase would be necessary for, in any furnace roasting galena bearing concentrate, the transport capacity must considerably exceed roasting capacity if smooth, efficient operation is to be obtained. The reasons for this are that the best roasting temperature is not far below the softening point of galena, and that hearth temperatures tend to rise with deepening of the mobile bed. If the furnace is being operated at near its full transport capacity a slight increase of feed rate, or delay in the routine of tooth cleaning will deepen the beds slightly, and the consequent rise of temperature may make the galena sticky; mobility decreases, teeth become dirtier, and in consequence of this vicious circle the hearth soon becomes seriously overloaded.

The functioning of the teeth was studied in all parts of the furnace and also in wooden model hearths constructed to scale and using dry sand and pigments. New teeth were designed for special purposes in different parts of the furnace; new combinations were worked out, and within a few months transport capacity was raised to over 100 tons per day. An average rate of 105 tons per 24 hr, nonstop, has been maintained for weeks on end, but the actual maximum transport capacity is uncertain, as there must always be some safety margin to guard against overloading. The above rates refer to operation at the normal column speed of 0.52 rpm; 120 tons per day has been reached at 0.61 rpm.

The first problem was the outward rabbling top hearth. The secondary concentrate carries 14 pct moisture, and having been filtered from a strong zinc sulphate solution, it has a very "sticky" stage during drying. The concentrate tended to reach the dropholes in this condition and grew and baked in the openings to the detriment of draught. As the cover arch is similar to an inward rabbling hearth, and the feed-hole is outside the gas offtake, the inner fifth of the first hearth was not being used. From immediately under the feed-hole inwards, one arm was dressed with narrow angle, short throw teeth, the remainder of this arm and all the other being dressed with narrow angle, long throw teeth in place of the original wide angle, short throw teeth. This arrangement caused feed to be spread over the central portion of the hearth; but as the inward throw is less than the outward throw there is no congestion. The arrangement is shown diagrammatically in Fig 4. The narrow angle permitted the concentrate to be moved more freely in the sticky stage and the long throw thinned the bed. Drying was now completed on the first hearth, and at most of the dropholes roasting had begun, so that a second sticky stage, caused by the presence in secondary concentrate of a small amount of elemental sulphur, had also been passed.

The second major problem was the congestion of the inward rabbling hearths, especially the most active fourth, mainly due to camber. Some alleviation was obtained by lengthening the inner teeth at the expense of making the immobile bed rather too thin to permit easy removal of hearth cake. The later, fully effective solution was the use of teeth with overlap across the whole cambered portion of the inward rabbling hearths. A subsequent modification was to reduce the number of overlap teeth in the eighth hearth and to eliminate them from the tenth to increase the depth of mobile bed and consequently the time of passage of these hearths. The reason for this is that it was observed, when the furnace was stopped for some hours except for a half-turn half-hourly, that the prolonged soaking greatly increased the penetration of the roast into the small aggregates which form very freely during the drying of secondary concentrate, owing to the zinc sulphate content. It is quite practicable to operate these lower hearths with lower transport capacity because galena is no longer present.

At higher loading rates spill from the inside of outward rabbling hearths increased. The teeth nearest the column on these hearths were elongated so that the leading edges of the blades almost touch the column.

The outward teeth most generally used in the Risdon furnaces have the following characteristics:

	Outward Teeth			Inward Teeth		
Throw—in.	6½	5	4*	8	6½	5
Spacing—in.	13	10	8	13	13	10
Angle of approach	32°	45°	30°	32°	32°	28°

* Designed for lower hearths but not yet installed.

Fig 4 shows, diagrammatically, the arrangements used in various positions.

Operation

Consistent roasting performance depends on regular feeding of an evenly graded concentrate, effective temperature control, clean rabbling and a smoothly running furnace.

Because of the characteristics of the feed components and the necessary arrangements for their delivery to the furnaces, the labor needed to obtain satisfactory feed control is much more than the average for other roasting plants. About half the feed consists of secondary concentrate delivered direct from a continuous disc leaf filter liable to vary from hour to hour in amount and from day to day in grade. The remainder, known as the "high grade" feed, is a mixture of screened dross and flue dust from the zinc melting furnaces with high grade zinc concentrate derived from any of four sources and with distinctly differing characteristics; this mixture carries from 26.5 to 28.5 pct sulphide sulphur whereas the secondary concentrate has from 21 to 24 pct. The general effects of this diversity of feed material are described in connection with furnace performance; as far as feed control is concerned it makes feeding at a constant tonnage rate entirely unsuitable. Effort must be directed at keeping the input of sulphide constant.

Secondary concentrate is weighed on a belt conveyor as it leaves the filter and begins its half-hour journey to the furnaces. The rate of high grade feed is adjusted hourly in accordance with the delivery rate and current grade of secondary concentrate. It is a cumbersome system needing conscientious operators but the sulphide input is consistently within 2 pct of the set figure, and adjustments of other major controls because of changes in effective input are not frequent.

Temperature control is maintained through the draughting and blast system. The following values are under regular observation and are logged hourly:

1. Gas temperatures in hearths 2, 3, 4, 5, 6, 8, 10, and column exit.
2. Furnace load (ammeter reading also continuously recorded.)
3. Blast pressure at column exit.
4. Draught between main damper and first hearth.
5. Sulphur dioxide in offtake gas (continuous recorder).

Control is exercised through adjustments of one or more of the following:

1. Furnace main damper: normal draught on the furnace side of the damper is 0.04 in., water gauge.
2. Blast fan damper: requisite settings for any given sulphur input are known and any need for departure from normal, as indicated by marked rise or fall of blast pressure at the column exit from the normal 0.5 in. w.g., is an indication of irregularity in rate or grade of feed.
3. Cold air by-pass damper: the fourth and fifth hearths are always fed with cold air in normal circumstances and hearths below the seventh with hot air; operation of the damper mainly determines the extent to which the sixth hearth receives cold air or hot. When regaining temperatures after a stoppage no cold air is fed to begin with but as temperatures rise an increasing amount is used.
4. The disc valves on blast ports: the three ports on any hearth are all opened to the same extent, and the close regulation of the temperature of each hearth is effected by variation of these openings as deemed necessary.

The current feed rate and the settings of all dampers and valves, as made, are recorded on blackboards mounted near the instrument panel.

The temperature objectives in autogenous and "higher sulphate"* roasting are:

	Autogenous	"Higher Sulphate"
Hearths 3 to 6	820°C	820°C
Hearth 8	770–780°C	800–820°C
Hearth 10	700–750°C	680–700°C

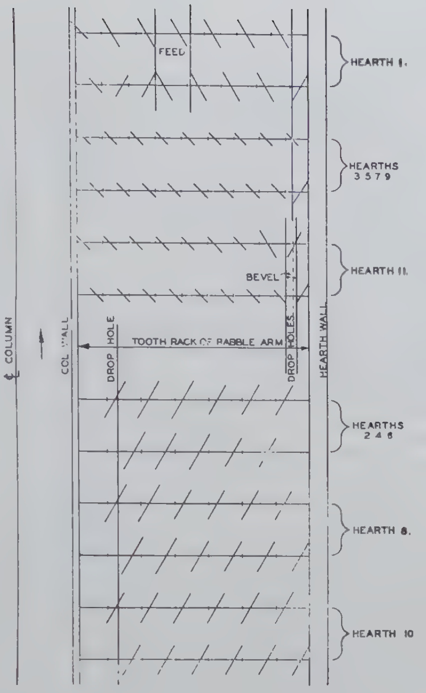

FIG 4—Tooth dressing.

The condition of hearths and teeth is examined at the beginning and toward the end of each 8 hr shift; where necessary a rough cleaning is carried out. During the main part of the shift the furnacemen start at the top of the furnaces and work down, cleaning all teeth thoroughly and also cleaning such of the arms, shields and portions of the walls and hearths as are allocated to them. The teeth in the lower hearths are changed once in a few months for inspection and for removal of any hard crust, but on hearths 3 to 6 they are changed every two weeks. This is made necessary by the presence of galena which has a significant vapor pressure at 850°C. Some volatilized lead sulphide comes in contact with the teeth, which are at a lower temperature because of the cooling of the arms, and condenses on them in a finely crystalline form, too adherent to be removed by the ordinary process of cleaning. The deposit occurs on the underside of the teeth as well as on the sides and soon causes a "drag" which raises the power input and will ultimately become sufficient to stop the furnace.

It is characteristic of all zinc concentrate roasting that the immobile bed cakes hard and if not broken up regularly begins to exert an excessive drag which will either break arms or stop the furnace. The treatment of these beds differs in practically all plants, and practice at Risdon has passed through several phases. Initially the hearths were barred or chiselled at intervals of several days. The work proved to be much less arduous, less material was removed and no more labor was required when the intervals were reduced, but it has been found preferable to fill the hearths to tooth level with coarse sand.

It was found impossible to maintain these beds intact; owing to changes of temperature in hearths, column and rabbles, to the disturbance caused by tooth cleaning and to the growth of galena "shoes" on teeth, the upper part of the sand is displaced and a crust of calcine is formed which behaves to some extent like ordinary hearth cake. These developments take time, however, and it has been found that a furnace can be maintained in free running condition provided the sand beds are renewed periodically. The fourth and fifth hearths are resanded every three months, and the other hearths every six months except the first which is done yearly when its teeth are inspected.

During the week before two hearths are to be resanded, they are chiselled thoroughly, the work being in the opposite direction to the rotation of the arms. The hearths done together (except in the case of the first hearth) are always an inward rabbling hearth and the one below it. The feed is cut off for one and a half hours. When material has practically ceased coming into the first hearth to be sanded, a few teeth are removed from the hearth above it and the furnace is restarted. Furnacemen at each door push material off the inward rabbling hearth at a steady rate until the hearth is clean. They then start to pull off the hearth below while sand is shovelled into the clean hearth—sufficient to form the immobile bed of two hearths—about 7 cu yd. As soon as the surplus sand has worked in from the outer part of the hearth the tynes are replaced in the hearth above. The one and a half hours allowed is ample, and it should be noted that, in the case of lower hearths, the feed will be on again long before the hearth cleaning starts. Temperatures are regained very rapidly and the furnace is usually normal within four hours.

After allowing for the cost of sand and of putting it in place, the wage saving resulting from the almost complete elimination of chiselling is not very great but the ultimate benefit from the reduction of wear and tear on the hearths and mechanism will be

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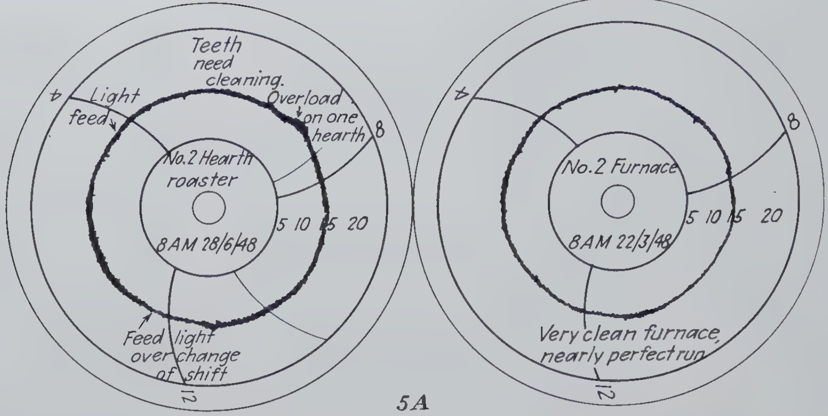
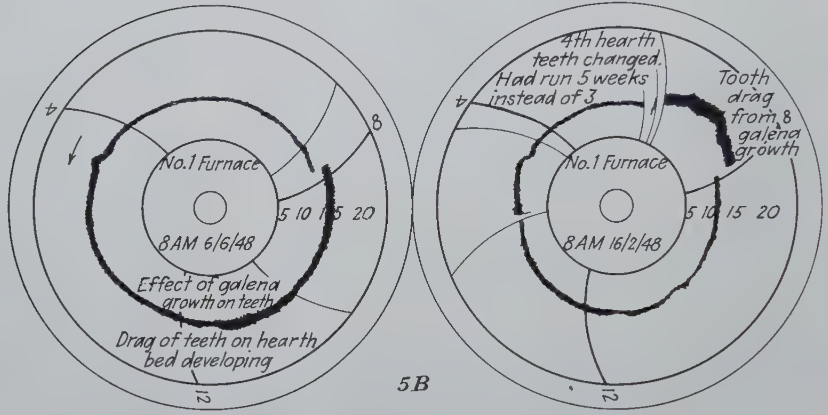
* See later in this section.



5A

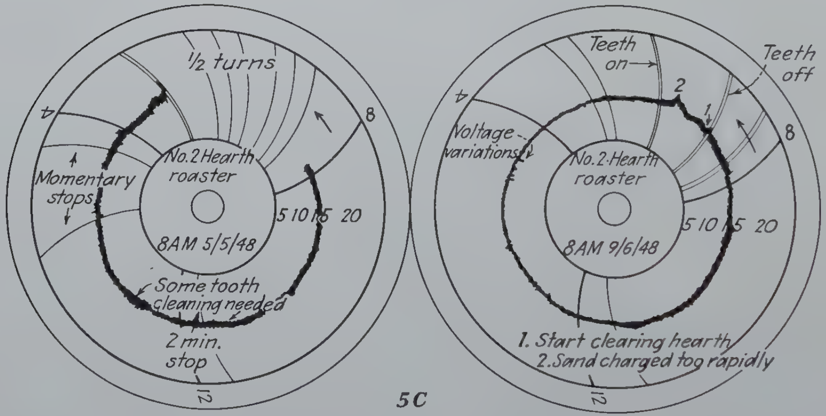
AN AVERAGE RUN

A VERY GOOD RUN



5B

EFFECT OF GROWTH OF GALENA ON BOTTOM FACES OF TEETH



5C

ROUTINE SHUT-DOWN

RE-SANDING OPERATION

FIG 5a—(Left) An average run. (Right) A very good run.
5b—Effect of growth of galena on bottom faces of teeth.
5c—(Left) Routine shut-down. (Right) Re-sanding operation.

quite considerable.

A recording ammeter gives invaluable guidance as to the general condition of the furnace and reveals irregularities or neglect unfailingly. Typical records are shown in Fig 5a, 5b, and 5c.

The furnace section must be closed down for about five hours once a fortnight to permit cleaning of gas fans. Auxiliary equipment is overhauled and every effort is made to have all maintenance work involving stoppage carried out at the same time; big jobs may extend the stoppage to eight hours, but these are infrequent now. Supplementary equipment is provided for disposing of the gas which is emitted at the feed-hole, and full feed is kept on the furnaces right up till shut-down time, but all blast valves are shut off earlier; column cooling air is reduced to a minimum and turned to atmosphere. Some air leaks into the furnace through rabble sockets, and the chimney effect of the furnace causes ingress of air to the lower half of the furnace wherever doors are not air-tight. Unless the column drive or bearing is being overhauled, the column is turned for one minute every half hour. This prevents the crusting of beds and presents new surfaces to the air available; a fair amount of roasting goes on, so that for several hours temperatures do not fall much except in the lower hearths where there is little sulphide available. A typical example of such temperatures is given in Table 1.

If the roasting is strictly autogenous, the recovery of the lower hearth temperatures is rather slow, taking about four hours for each hour of shut down, unless calcine grade is sacrificed to a serious extent. If an oil burner is used at Hearth 9 to assist recovery, the time is reduced by half at an expenditure of about 6 gal of oil per furnace per hr, and calcine grade does not suffer appreciably.

If a stoppage extends beyond eight hours for external reasons the furnaces are then run and fed for five minutes in every thirty or forty. This retards further temperature drop almost completely. If the bottom hearth becomes seriously overloaded, it may be relieved by discharging into the basement.

The addition of the cyclone dust from both furnaces to the middle hearths of one furnace results in about 100°C drop in bed temperature and necessarily affects roasting rate. The lowering of feed grade resulting from the addition of dross also causes a drop in roasting performance. It was decided to abandon strictly autogenous roasting, therefore, and use a small oil-burner on each furnace as required, to help restore temperatures after the furnace stoppages and to make good the effect of cyclone dust addition. Experience shows that the burners are used to best advantage in the ninth hearth, and consumption of fuel oil amounts to about 0.15 pct on the material roasted or about 0.7 pct on the sulphur oxidized.

Additional fuel oil has been used during most of the last year in order to increase the formation of sulphate, which is done by reducing the sulphide much below the level attainable with autogenous roasting at high feed rates. The temperature objectives have been given earlier in this section, and the consumption of fuel oil is shown in Table 6.

Equipment designed for the changing of rabble arms and teeth is very satisfactory and good team work has developed in its use. Where changing is frequent the set of teeth on an arm is removed and replaced in 3–5 min.

Lost time was very heavy initially.

Table 1 . . . Gas Temperature °C during Stoppage

Time	Hearth 2	Hearth 4	Hearth 6	Hearth 8	Hearth 10
9 a.m.	780	830	810	760	650
11 a.m.	760	820	800	720	580
1 p.m.	740	810	760	640	510
3 p.m.	740	810	750	590	450

Furnace stopped 8 a.m.

Table 2 . . . Furnace Stoppage Analyses

Analysis Headings	Percentage Loss of Furnace Time					
	1943–4	1944–5	1945–6	1946–7	1947–8	Objective
Feed and calcine conveyors		1.06	0.60	0.72	0.48	Nil
Gas disposal, power, etc		1.03	0.55	0.60	0.55	Nil
Routine shut down		4.87	3.83	2.80	1.92	1.5
Furnace work including changing arms, shields, teeth and renewal of sand beds		2.12	1.29	1.19	1.04	0.75
Renewal of column bearing					1.05	
Total lost time pct	10.8	9.08	6.27	5.31	5.04	2.25

Table 3 . . . Assays of Concentrates

Assay Pct	B.H.N.* (a)	B.H.S.* (a)	B.H.Z.* (a)	Mixed B.H.		Rosebery		Risdon	
				(b)	(c)	(a)	(d)	(e)	(d)
Zn	52.2	53.10	52.5	51.1	49.0	54.4	55.5	49.7	49.65
Pb	1.3	1.1	1.6	1.1	1.3	3.7	2.0	1.6	0.9
Mn	1.58	1.4	1.42			0.14		1.0	
Cu	0.08	0.07	0.11	0.109	0.118	0.51	0.295	0.23	0.20
Cd	0.22	0.168	0.189	0.201	0.196	0.137	0.139	0.69	0.64
Fe	9.91	8.32	8.76	9.3	8.8	5.9	6.05	8.1	9.4
T/S	31.83	32.00	31.74	30.97	29.34	32.7	32.50	23.7	24.0
SO_4/S				0.43	1.06	0.16	0.23	1.7	1.47
S/S				30.54	28.28	32.54	32.27	22.0	22.53
H_2O	8	8	8	8	8	8	8	14	14.5

(a) Mill production, year ended June 1942.
(b) Mainly current material delivered to furnaces, year ended June 1948.
(c) Deliveries mainly from storage dumps, year ended June 1948.
(d) Deliveries to furnaces, year ended June 1948.
(e) Deliveries, 4 weeks ended 22nd Sept. 1943.
* Broken Hill North, Broken Hill South, and Zinc Corporation.

Table 4 . . . Laboratory Roasting Tests

	B.H.N.* (a)	B.H.S.* (a)	B.H.Z.* (a)	Rosebery. (b)	Risdon (b)	Ros.-Ris. (c)
Assays pct						
Total Sulphur	31.35	31.27	31.46	32.55	24.9	28.7
Sulphate Sulphur	0.12	0.15	0.16	0.25	1.7	0.95
Sulphide Sulphur	31.23	31.12	31.30	32.3	23.2	27.75
Zinc	50.7	52.5	52.0	54.5	48.5	51.5
Sizings pct (Tyler)						
+100	4.55	20.1	24.75	2.6	0.2	
+150	16.3	20.6	18.4	3.4	1.5	
+200	16.2	12.7	9.9	8.9	6.7	
+250	9.0	5.9	4.2	7.8	7.0	
−250	53.95	40.7	42.75	77.3	84.6	
Sulphur oxidation rate, lb per sq ft per day (to 4 pct S/S)	16.9† 17.4‡	14.8 17.1	13.4 16.5	16.9 18.2	12.65 15.8	15.75 17.7
Sulphation Levels						
Pct SO_4/S with S/S at 8 pct	0.37	0.48	0.46	0.62	1.57	1.11
Pct SO_4/S with S/S at 6 pct	0.48	0.63	0.56	0.74	1.80	1.28
Pct SO_4/S with S/S at 4 pct	0.66	0.90	0.73	0.96	2.12	1.54
Pct SO_4/S with S/S at 2 pct	1.08	1.35	1.04	1.65	2.60	2.15

(a) Mill production samples, early 1943.
(b) Deliveries to furnaces, week ended 16th June 1943.
(c) Mixture in equal parts of concentrates marked (b).
* See footnote, Table 3.
† Roasting in muffle without chimney.
‡ Roasting in muffle with chimney.

Table 5 . . . Percentage of +250 Mesh (Tyler) Material in Feed Components

Four weeks ending	Broken Hill Mixture			Rosebery			Risdon		
	Av.	Max.	Min.	Av.	Max.	Min.	Av..	Max.	Min.
2/4/47	42.9	53.6	28.2	15.8	25.2	11.9	37.6	46.5	24.9
30/4/47	44.4	51.0	36.6	18.5	38.2	10.8	30.3	41.2	18.3
28/5/47	48.3	56.2	40.8	18.7	27.1	15.8	32.4	46.6	19.3
25/6/47	52.4	58.3	48.5	18.8	31.8	16.2	27.6	36.9	20.0
23/7/47	50.3	59.4	44.4	19.1	21.0	15.8	27.1	32.8	16.4
20/8/47	43.3	49.3	37.8	17.9	25.2	14.3	31.6	45.8	19.8
17/9/47	42.3	47.7	38.0	17.9	26.7	14.0	31.0	54.6	15.7
Av.	*46.3*			*18.1*			*31.1*		

To a large extent this was caused by blockage or breakdown of auxiliary equipment much of which was 20 yr old, but there were many short stoppages in connection with furnace work. Much effort was concentrated on eliminating causes of trouble and the progress made is shown in Table 2.

The final column gives the minimum times in which it is considered possible to carry out essential operations such as fan cleaning, teeth changing and renewal of sand beds.

Roasting Characteristics of Feed Components

The feed to the furnaces is always a mixture of concentrates from any or all of four sources, three Broken Hill mills and the Company's own mill at Rosebery, together with secondary concentrate (called Risdon) recovered from leached calcine residues, and latterly about 5 pct of dross and flue dust from zinc melting furnaces. (See Table 6.) Since feed composition inevitably varies, a knowledge of the roasting characteristics of the different components and mixtures is essential.

The objectives are not constant. The requirements of the zinc plant as a whole, the position in regard to stocks and certain subsidiary operations lead to variations in the stress laid on obtaining maximum oxidation of sulphides which is incompatible with relative completeness of oxidation and production of sulphate.

Table 3 gives analyses of typical samples of the five concentrates. In the Broken Hill concentrates the iron is largely present as the zinc-iron sulphide, marmatite, whereas in Rosebery concentrate there is both zinc-iron sulphide and pyrite; and in Risdon concentrate the iron is present partly as oxide but principally as zinc ferrite. Lead is present as galena in the primary concentrates but as sulphate in Risdon concentrate while the latter also contains a little elemental sulphur.

The gross thermal values of the concentrates on complete oxidation, as calculated from analyses (a), (d) and (e), Table 3, range from 1180 to 1150 C.H.U. per lb for the Broken Hill concentrates and are 1125 and 720 C.H.U. per lb for Rosebery and Risdon concentrate respectively. Particle sizes are more important than minor differences in gross thermal value in influencing roasting rate, and relative roasting rates for the various dried concentrates have been studied under controlled conditions in the laboratory (by E. Z. Research Department).

An iron roasting dish with a false bottom was used in an electrically heated muffle with and without a small exhaust chimney, and temperature was closely controlled throughout. A half inch bed of material was well rabbled every five minutes and the most difficult concentrate was dead-roasted in 2 hr at 800°C under these conditions. In all cases roasting was faster at a bed temperature of 800°C than at 750 or 850°C, and the rates for the various concentrates always fell in the same order. Sulphate is formed to any extent only when sulphide content is relatively low, and under these conditions is more prevalent in the coarse fraction containing aggregates than in −10 mesh material. Rosebery and Risdon concentrates sulphate much more readily in both coarse and fine fractions than the Broken Hill materials. Table 4 gives assays, sizings, roasting rates and sulphate formation in the tests described and it should be noted that, in general, the progressive or instantaneous isothermal roasting rate for any concentrate is directly proportional to the progressive sulphide concentration and to a proportionality factor which is characteristic of the material and of the conditions of the roast.

The sizing relationships are perhaps more clearly expressed through the specific surfaces as determined by the Fisher sub-sieve sizer; typical concentrate samples gave the following results:

	Specific surface
B. H. North	740– 810 sq cm per g
B. H. South	680– 710 sq cm per g
B.H. Zinc Corporation	545– 600 sq cm per g
Rosebery	1310–1520 sq cm per g
Risdon	1940 sq cm per g

For the several Broken Hill concentrates, the ratios of specific surface and roasting rates are close enough to indicate some connection, and it can be assumed that the low grade of the Risdon concentrate tends to offset the advantage of its fineness. The rates for Rosebery concentrate are not nearly as high as its fineness would lead one to expect. The explanation is to be found in its high galena content. It ignites much more rapidly than the others and roasts so actively that it is almost impossible to prevent fusion of galena which makes the roast become "sticky" and "ball-up."

The same facts explain why the Rosebery-Risdon mixture has better rates than the averages of the rates of the components. The ready ignition of the Rosebery concentrate gives the roast a good start, while its high activity which tends to run temperature out of control is moderated by the low grade material.

Experimental roasting times are well borne out in practice. It is impossible to get satisfactory results with mixtures containing much Broken Hill concentrate at above the normal speed of furnace column. With Rosebery-Risdon mixture the speed may be raised from 0.52 rpm to 0.615 rpm, an increase of 18 pct.

While the sizings of the various concentrates are fairly consistent when long term samples are examined, there is a by no means insignificant day to day variation. Table 5 gives a clear indication of the extent to which these variations are experienced.

Performance

The complete performance record of the furnaces has been summarized in Table 6 and shown graphically in Fig 6. In this summary, the results have been arranged for periods of varying length, each period having some common feature which more or less determined or characterized the performance. The reference letters in the table and graph refer to the following explanations of the grouping:

A. The first four-weekly period during which furnace crews were becoming accustomed to the equipment, and initial difficulties were being overcome.

B. A period during which it was apparent that roasting capacity exceeded hearth transport capacity, and the lower hearths were doing very little roasting. Efforts were made to raise the temperatures of the hearths by "split drafting." Gas offtakes were connected to the bottom hearth, and from Hearth 7 the furnace was drafted downward. The temperatures of the lower hearths improved, but drying was slower and the activity of the upper hearths decreased. With a drier and higher grade feed, very active on the upper hearths, the method has definite advantages, but feed grade was tending to fall.

C. The effect of hearth camber was reduced by deepening the inner teeth of inward rabbling hearths, and column speed was increased from 0.52 to 0.61 rpm. More feed was handled and

Table 6 . . . Performance

Reference	A	B	C	D	E	F	G	H	J	K	L	M
Number of weeks ended.	4 7.4.43	20 25.8.1943	20 12.1.1944	8 8.3.1944	44 10.1.1945	20 30.5.1945	24 14.11.1945	40 21.8.1946	4 18.9.1946	44 23.7.1947	20 10.12.1947	24 26.5.1948
Furnaces operated......	1	1	1	1	2	2	2	2	2	2	2	2
Cyclone dust returned..	No	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes
Feed Composition Pct												
Rosebery Conc.......	49.7	51.5	38.5	25.5	29.6	7.9	22.5	9.9	22.4	12.0	23.4	22.2
Broken Hill Conc....					5.1	27.1	19.3	39.0	30.4	32.8	28.5	21.3
Dross, etc...........			0.4		0.8		0.8	1.0	7.4	5.0	4.9	5.4
Risdon Conc.........	50.3	48.5	61.1	75.5	64.5	65.0	57.4	50.1	39.8	50.2	43.2	51.1
Feed												
Tons per furnace per day..............	61.3	64.7	75.0	92.7	72.8	80.0	80.3	93.8	76.1	92.7	88.0	93.8
S/S Pct............	27.2	27.8	26.0	25.25	25.8	25.8	26.2	26.4	25.8	25.4	26.2	24.7
Lb S per sq ft per day												
Input...............	11.6	12.44	13.5	16.2	13.0	14.6	14.6	17.2	13.6	16.3	16.0	16.1
Oxidized............	9.4	11.1	11.9	13.2	11.3	11.25	12.6	14.4	11.4	13.2	14.0	14.6
S oxidation Pct......	80.6	89.2	87.9	81.5	86.7	78.6	86.4	83.6	83.3	80.8	88.0	90.8
Calcine Assays												
SO_4/S Pct..........	2.09	3.38	3.08	2.36	2.48	1.36	1.76	1.33	1.63	1.22	1.52	1.68
S/S pct.............	5.76	3.29	3.46	5.15	3.74	6.11	3.92	4.80	4.71	5.38	3.51	2.50
SO_4/S formed												
Tons per furnace per day..............	1.16	1.98	2.11	1.98	1.64	0.98	1.28	1.12	1.13	1.02	1.22	1.44
Fuel Oil used												
Pct of S oxidized.....											1.54	2.19
Stoppages												
Lost time Pct........	10.4	9.7	11.7	10.4	10.2	8.15	5.95	5.7	6.3	5.1	4.6	3.7

temperatures in the lower hearths improved.

D. Teeth with longer throw, giving overlap, were introduced on the inner half of inward rabbling arms. Higher feed rate resulted and the greater roasting capacity of the furnaces, even with a very low grade feed, was clearly demonstrated.

E. The second furnace came into operation, and the gas disposal system which was shared with two other furnaces proved inadequate for the operation of both the new furnaces at the higher roasting rate achieved in the previous period.

F. One of the other furnaces was shut down, and draught improved but appreciable quantities of B.H.S. and B.H.Z. concentrate were introduced for the first time, and considerable difficulty was experienced in producing an acceptable grade of calcine. Column speeds were restored to 0.52 rpm and were even reduced to 0.46 rpm for part of the period, but for no month did calcine average below 5.5 pct S/S.

G. During this period the feed mixture varied several times, the high grade portion being alternately all Rosebery and all Broken Hill concentrate, but the several changes afforded opportunities for close comparison of techniques. Traverse rates were reduced in Hearths 8 and 10, and calcine of under 5 pct S/S was eventually produced from Broken Hill-Risdon mixture, with a roasting rate of 12.5 lb S per sq ft per day which was then regarded as the acceptable minimum.

H. New supplies of Broken Hill concentrate contained no B.H.Z. and were mainly B.H.N. No difficulty was experienced in increasing roasting rates to 14.5 lb S per sq ft per day, even when there was no Rosebery concentrate present and while maintaining calcine at less than 5 pct S/S.

J. A four-week period during which shortage of concentrate occurred and the furnaces were run, for a time, on the minimum load at which temperatures could be maintained. During this feed shortage the last of the old furnaces was shut down, and it became necessary to include zinc melting furnace dross and flue dust in the roaster feed to the extent of about 5 pct. Dust from the cyclones, formerly roasted in the old furnace, now had to be returned, at first to the feed though soon afterwards provision was made for delivering it to the middle hearths of No. 2 furnace.

K. This period was, in most respects, a continuation of period *H*, but marked by the dilution of the feed with dross and the effect of returning cyclone dust, which combined to reduce roasting rate from 14.4 to 13.4 lb S per sq ft per day. The admixture of dross with concentrates results in more rapid hardening of hearth beds and quicker fouling of teeth. Fortunately the developmental work on sand beds had been completed and both furnaces were soon bedded throughout. The labor saved from hearth cleaning was more than enough to enable better attention to be given to tooth cleaning.

The dust addition reduced the middle hearth temperatures of No. 2 furnace and therewith the roasting rate. Continuous addition at one point causes a drop of 100°C in bed temperature, but as the addition was spread over two hearths, the effect of the dust was not so sharply evident in temperatures. The most noticeable effect was in calcine assays, those of No. 2 furnace being consistently about 1 pct S/S higher than those of No. 1 in spite of adjustment of feed distribution to insure equal overall sulphur inputs to the two furnaces.

The higher calcine assays, now tending to be just over the acceptable 5 pct S/S, prevented any attempt to restore sulphide input by increasing feed rate to make up for the dilution. Excluding from period *K* four weeks during which 40 pct of the feed was B.H.Z. concentrate, and calcine went to 8 pct S/S, the effects of dross and cyclone dust can be fairly assessed over two comparable 40 week periods. The feed rates were nearly equal, 93.8 and 92.6 tons per furnace-day respectively.

Dilution caused sulphur input to fall from 17.2 to 16.4 lb per sq ft per day. Temperature reduction by dust caused oxidation efficiency to fall from 83.6 pct to 81.6 pct so that sulphur oxidized fell from 14.4 to 13.4 lb per sq ft per day. The chief effect is caused by dilution, though it may not be immediately clear why, with a lower sulphide input, the oxidation efficiency should not be expected to increase.

The reason is that, in autogenous roasting, maintenance of temperature and of the limited roasting rate in the lower hearths is dependent on the carriage of sufficient amounts and concentrations of heat and sulphide in the calcine from the middle hearths, and on close control of air input. The addition of cyclone dust to the middle hearths affects the balance; calcine temperature is reduced while more sulphide is carried down. The latter can be corrected, as was done, by feed ad-

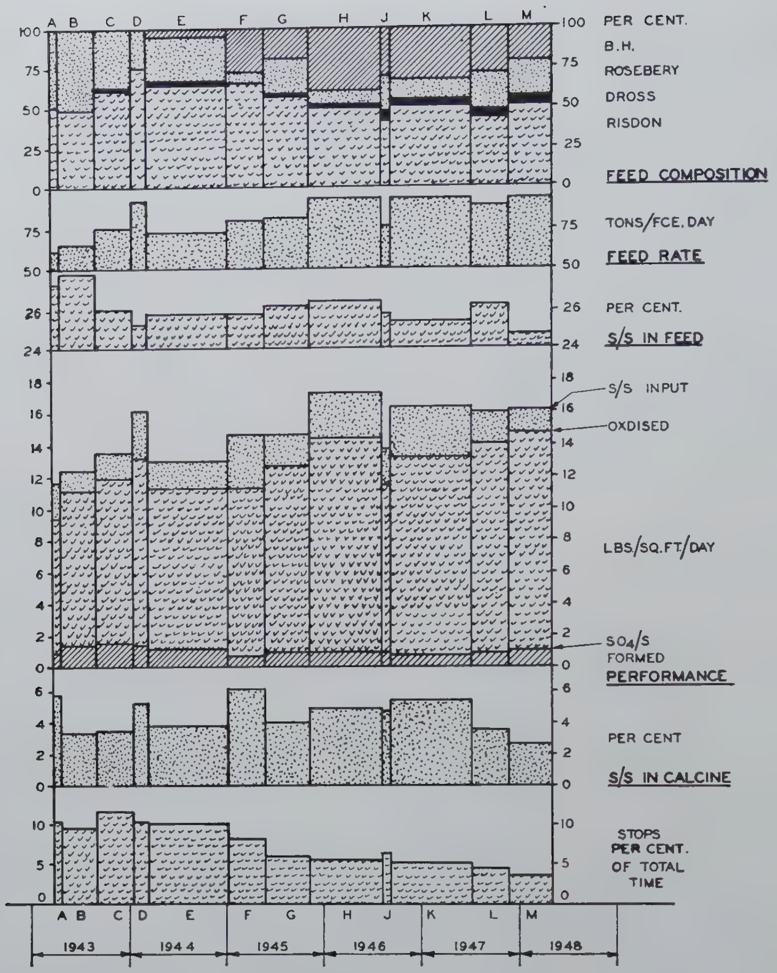


FIG 6—Performance data.

justment, but the temperature effect cannot be remedied without use of extraneous fuel.

On the upper middle hearths, where the roast is most active, it is usually necessary to depress that activity by use of cold air in order to avoid overheating. Even low grade concentrates are more than sufficiently active and by increasing input it is possible, up to a point, to maintain oxidation rate on these hearths. The limit is reached when the amount and concentration of sulphide passing to the lower hearths tend to get out of balance.

By comparing the work of different months in periods *H* and *K*, in which feed grade and sulphide input are nearly the same, it is found that the effect due to cyclone dust addition is only one-third of that due to dilution by dross, that is, about 25 pct of the total decrease of 1 lb per sq ft per day.

It appears, then, that the dust addition is being made too low in the furnace, and that it should be made in the zone in which depression of activity is required. Gas velocity through the dropholes is so high in this zone however that return of dust to it would cause a large circulating load to build up. The dust is added to the moderately active sixth and seventh hearths.

L. It was decided to make use of small oil-burners to overcome the temperature drop due to cyclone dust in No. 2 furnace and to hasten recovery of both furnaces after long stoppages. At the time the burners became available there was a demand for an increase of sulphate formation and as this increases with decrease of sulphide, it was decided to operate the burners more or less continuously to stimulate roasting in the lower part of the furnace.

A short test was made to determine the consumption of oil for the original purposes; it was 0.17 pct of the tonnage roasted or 0.75 pct of the sulphur oxidized. To stimulate sulphate production, about three times as much is used. The most effective position for an oil burner was found to be the ninth hearth.

Table 7 . . . Autogenous vs. Moderately Assisted Roasting

Duration	Period *K*, Best 24 Weeks of 44	Period *M*, Consecutive 24 Weeks
Feed rate, tons per furnace per day	93.2	93.8
Feed grade, pct S/S	25.7	24.7
Sulphide input, lb per sq ft per day	16.6	16.1
Sulphide oxidized, lb per sq ft per day	13.7	14.6
Sulphur oxidation pct	82.6	90.8
Calcine assay, pct SO_4/S	1.30	1.68
Calcine assay, pct S/S	4.94	2.50
Fuel oil used pct of S oxidized		2.19

M. The experimental work on the application of fuel oil being completed and good supplies of high grade concentrates being available to give a regular feed mixture, the furnaces settled down to a long run of extraordinarily consistent performance. Both the quick recovery from the fortnightly stoppages due to the use of fuel oil and a greater stability of furnace crews than existed in wartime and immediately afterwards, contributed to these results. By way of making allowance for the latter factor in comparing periods *K* and *M*, the best 24 weeks' work in the former period has been selected to compare with the 24 consecutive weeks' work of the latter; the results are given in Table 7.

The benefits derived have been calculated on the basis of 90 pct of unroasted sulphide being recovered as secondary concentrate from calcine leach residue and are found to be, for each ton of fuel oil used:

2.69 tons sulphur oxidized,
2.24 tons sulphuric acid, equivalent of extra sulphate formed,
1.34 tons of high grade concentrate (32 pct S/S) saved,
18.5 tons of low grade concentrate (22.5 pct S/S) which does not have to be returned for roasting.

The last item in this saving is more important than it may seem at first sight; it means not merely a decrease by one-sixth in the secondary concentrate to be treated by the furnaces, but it effects an increase of 0.6 pct in a feed grade already uncomfortably low for the maintenance of high roasting activity. That this increase was not actually obtained was due to a greater intake by the zinc plant of less well roasted calcine from other sources.

Heat Balances and Gas Tenors

Some heat balances were made in 1944 and showed radiation losses slightly in excess of 20 pct of the heat input. The work was done under great practical difficulties, including irregular operation, and there is some reason to believe that the loss is scarcely so high; but whether the actual loss is 10 pct or 20 pct is immaterial to the discussion of gas tenor in relation to heat balance which follows.

In Table 8 there are shown three balances calculated from recent performance figures, and average gas tenors, and an assumed radiation loss which is proportional to average furnace temperature, using the observed figure of the 1944 balances as basis. To simplify presentation, heat contents have been referred to atmospheric temperature instead of the more usual 0°C.

Table 8 . . . Heat Balances

Condition (see below)	Per Hour for Two Furnaces					
	(*A*)		(*B*)		(*C*)	
	C.H.U. × 10^3	Pct	C.H.U. × 10^3	Pct	C.H.U. × 10^3	Pct
Input						
Oxidation of concentrate	13,371	100.0	14,449	94.1	15,353	98.1
Combustion of Fuel Oil			900	5.9	300	1.9
Totals	13,371	100.0	15,349	100.0	15,653	100.0
Outgo						
In calcines	1,403	10.5	1,205	7.8	1,580	10.1
In water vapor, ex conc.	1,700	12.7	1,559	10.2	1,759	11.2
In water vapor, ex air	99	0.7	130	0.8	124	0.8
In dry gases	7,181	53.7	9,474	61.7	9,167	58.5
Loss from dust returned	47	0.4	56	0.4	56	0.4
Radiation loss	2,941	22.0	2,925	19.1	2,967	19.0
Totals	13,371	100.0	15,349	100.0	15,653	100.0
Conditions						
Fuel oil used, tons per day			0.92		0.31	
Feed rate, tons per day	186		176		203	
Feed, pct moisture	10.9		10.5		10.5	
Feed assay, pct S/S	25.7		26.3		26.0	
Calcine assay, pct S/S	5.0		2.54		4.32	
Calcine assay, pct SO_4/S	1.3		1.78		1.4	
Calcine discharge, °C	677°		617°		697°	
Gas volume, N.T.P., cfm	13,200		16,500		16,500	
Gas offtake temperature °C	450°		470°		450°	
Offtake gas, SO_2 pct	5.0		4.2		4.5	
Sulphur oxidized, lb per sq ft per day	13.7		14.6		15.6	
Sulphur eliminated, lb per sq ft per day	13.5		14.2		15.3	

The conditions chosen for these balances are:

A. The best 24 weeks performance for autogenous roasting of mixtures including dross, as shown in Table 7.

B. The comparable performance when using some fuel oil continuously to improve sulphate formation, also as shown in Table 7, except that feed grade is raised to that which would have resulted had other calcine received by the zinc plant remained of the same grade as in the first period.

C. Performance when using fuel oil only intermittently to make good losses of temperature due to stoppages and the introduction of cyclone dust. The furnaces have been operated under this condition for a short time only but actual performance has been slightly better than that assumed for Table 8.

The amount of heat radiated does not vary much and so a larger fraction of the heat must be carried away by the gases when the space rate of roasting is increased. The upper temperature of the gases is limited to that which gives the fastest roasting and consequently an increase in the space rate must be accompanied by a fall in gas strength. It is nevertheless true that the whole of the heat input to the furnace could be carried by better grade gas than is actually being made, and without exceeding the maximum desirable temperature of 820°C. As low gas tenor is the chief disadvantage of hearth roasters in comparison with flash roasters it is worth examining why the gas from these furnaces is so low.

In the first place an open feed-hole and main damper slot together account for a dilution of at least 10 pct. Secondly, activity is so great on the fourth hearth that 20–25 pct of the roasting is done there and an excess of air must be used to prevent the desired temperature being exceeded. Finally, in the lower hearths hot air is used as blast and this air can never attain the same percentage of sulphur dioxide as the cold air input because of the imposed maximum temperature.

Apart from the sealing of the feed-hole, the grade of gas produced could be increased by moving the material much more quickly over the most active hearths and much more slowly over the lower hearths. Differential rabbling rates are already being used in these furnaces almost to the limit of practical convenience but with furnaces having three or four arms per hearth greater differentiation is possible and it is by no means certain that the hearth roaster will be finally outmoded by the flash roaster.

References

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El Paso Slag Treatment Plant

T. J. WOODSIDE*

Prior to 1927 the lead blast furnace charge at El Paso consisted principally of direct-smelting carbonate ores, very low in zinc, and the resulting slag seldom carried more than 4.0 pct. With the exhaustion of the mines in Northern Mexico which supplied these ores, they were supplanted with a much smaller tonnage of sulphide concentrates containing appreciable amounts of zinc, and the zinc content of the slag rose to 10.0 pct.

The Anaconda Company's slag fuming plant at East Helena, Montana, had then been in successful operation for several years, and it was immediately recognized that, while at that time the production of high zinc slag was small, if the grade held, a plant for the recovery of zinc from the accumulated slag might some day be practical. The grade not only held but became increasingly higher so that by 1946 sufficient slag had been accumulated to warrant the construction of a fuming plant regardless of future slag production from the blast furnaces, and with the removal of Government restrictions on construction at the end of the war the project was undertaken.

The general design of the plant follows that at Bunker Hill, with waste heat boiler, unit coal pulverizers and even more extensive instrumentation and automatic control.

The area around the lead blast furnaces is rather congested, being cut off from the nearest feasible site for the fuming plant by the copper plant, so that the most practical route for hot slag transfer is through the converter aisle. For this reason and also to make use of the existing converter cranes to serve the fuming furnace, an unused reverberatory at the north end of the converter building was dismantled and the fuming furnace and boiler located in its place. A flue at right angles to the furnace and boiler runs northward to the U-tube coolers and baghouse (Fig 1). From the baghouse a steel flue runs eastward to an existing and long unused 300 ft concrete stack. The coal handling system and de-leading plant lie north of the furnace and east of the cooling tubes and baghouse.

The furnace is conventional, 8 × 21 × 33 ft high inside and completely water jacketed (Fig 2). There are 21

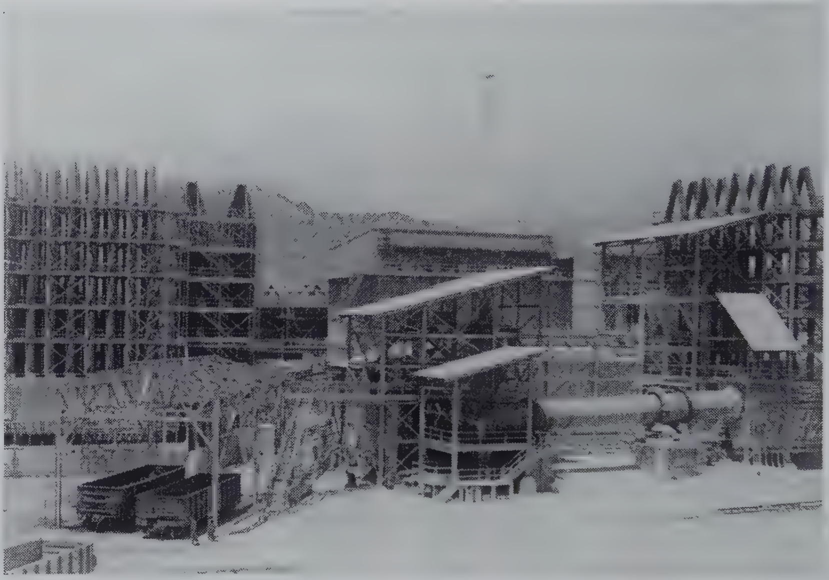

FIG 1—U-tube coolers, baghouse, and de-leading kilns.

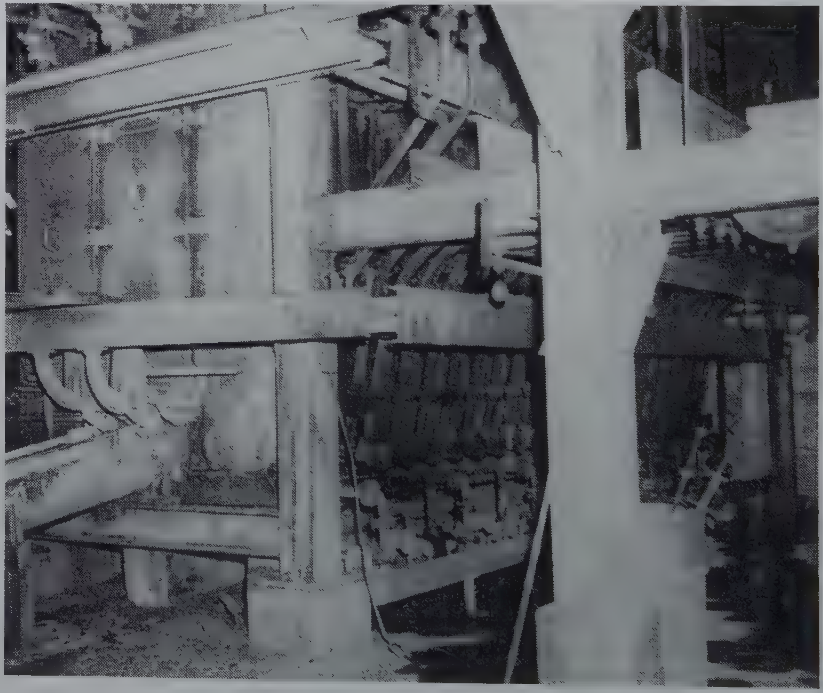

FIG 2—Fuming furnace.

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TP 2651 D. Discussion of this paper (2 copies) may be sent to *Transactions* AIME before October 1, 1949. Manuscript received Jan. 26, 1949; revision received May 13, 1949.

* Superintendent, El Paso Smelting Works, El Paso, Texas.

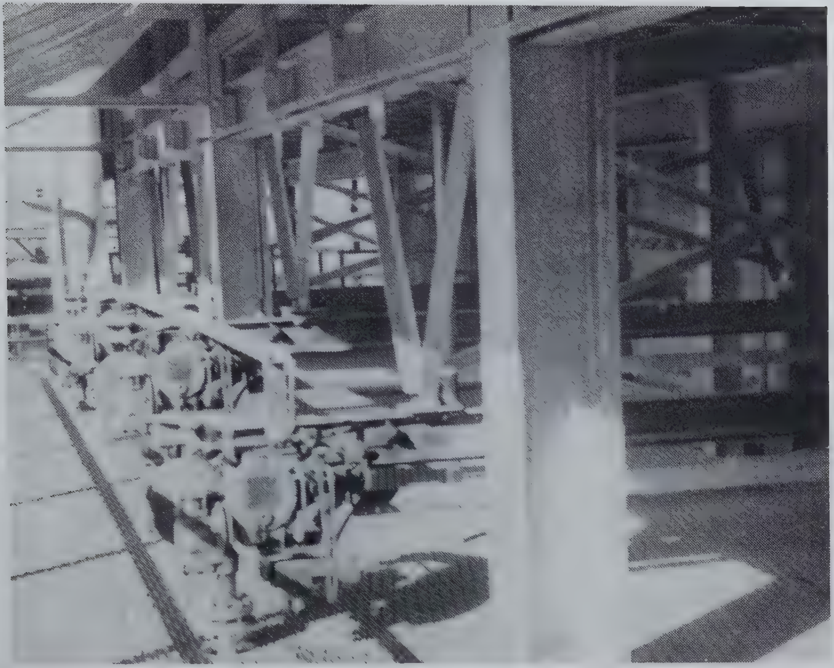

FIG 3—Soot blowers.

double-inlet tuyeres on each side of the furnace, with center line of tuyeres 5½ in. above the furnace bottom, and tuyere pipes extending 7 in. inside the furnace. Tuyere pipes were originally water jacketed, but since these proved to have very short life they have been replaced with 3½ in. od × 1½ in. id hydraulic tubing. Slag is tapped through two 5 in. water jacketed tap holes simultaneously into two 300 cf air dumped slag pots.

A water jacketed flue connects the furnace to the water-wall combustion chamber of the B. & W. two drum sterling type boiler which is rated at 72,000 lb of steam per hr at 400 lb pressure and 700° total temperature. Combustion chamber, boiler and economizer are equipped with a total of 35 fully automatic Diamond soot-blowers, Fig 3, operating on compressed air. The soot-blower installation has been very satisfactory, no hand lancing being required to keep tubes free of fume. Two motor driven A B C fans, each rated at 51,000 cfm, and connected in parallel, deliver gases from the economizer outlet to a 7 ft diam balloon flue leading to the U-tube coolers. Furnace draft is automatically controlled by louvre dampers in the fan inlets. The U-tube coolers are in two banks, each bank consisting of forty 30 in. × 58 ft tubes. Additional cooling is supplied when required by an automatically operated damper which admits air into the gases as they leave the U-tubes. A second pair of fans with capacity of 75,000 cfm each and automatically dampered like the boiler fans deliver gases to the baghouse.

The baghouse is constructed entirely of concrete, including roof and thimble floor, and is divided into seven chambers each containing 160 18 in. × 30 ft woolen fume bags. Six chambers are used to collect zinc fume from the furnace gases and the other collects lead oxide fume from the deleading kilns. The bags are shaken automatically when the pressure differential across the bags reaches a predetermined maximum, the chambers being shaken consecutively until the pressure drops to the desired minimum. In order to keep a slight draft on the inlet side of the baghouse, and thus prevent leakage of fume through screw conveyors, the outlet flue is evacuated by a Sirroco type induced draft fan with a capacity of 180,000 cfm, delivering gas to the stack.

Combustion chamber, boiler, economizer, balloon flue, U-tubes and baghouse chambers are equipped throughout their length with screw conveyors which operate continuously and discharge fume into a system of drag and belt conveyors which carry it to the de-leading plant.

Washed 1 × 0 in. slack coal from Dawson, New Mexico, is dumped into a track hopper. Coal analysis is approximately as follows:

Ash	Volatile	Fixed Carbon	Btu
12.0	38.0	49.00	13,000

From the track hopper, coal is passed through a hammer mill and is pneumatically conveyed to a 300 ton storage tank. A Merrick Feedoweight delivers coal from the tank to a Redler elevator and rotary conveyor which distribute it to the three 30 ton pulverizer bins. The pulverizers are B. &

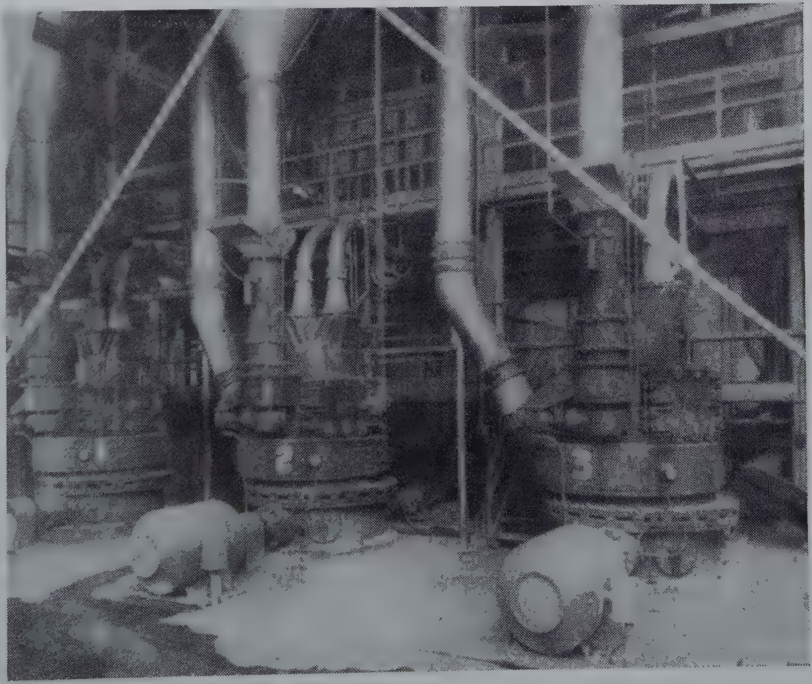

FIG 4—Coal pulverizers.

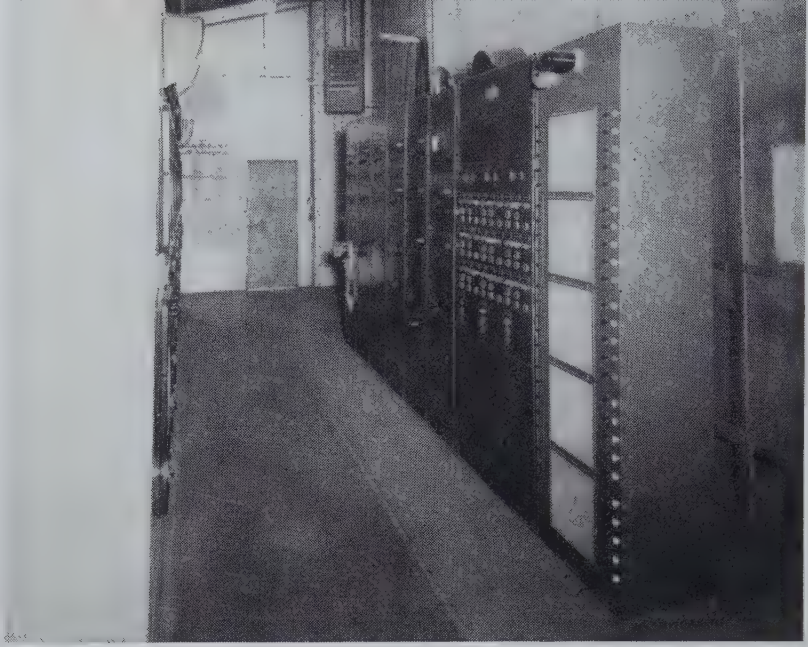

FIG 5—Control panel.

W. type E, size 47, two being operated with the third in reserve (Fig 4). Furnace blast is supplied by an Elliott turbine driven blower with a capacity of 18,000 cfm at 10 lb. The blast is divided by automatically operated butterfly dampers into primary and secondary air. The primary air passes through the pulverizers, picking up the coal and carrying it to the primary inlets of the tuyeres. The secondary air goes directly to the tuyeres. A 15,000 cfm motor driven blower was installed to inject low pressure air through a number of 2½ in. pipes into the upper part of the furnace and the crossover flue to oxidize completely all coal and metallic zinc. This was found to be unnecessary, however, as furnace draft pulls in enough air through the charging hole, and the blower is no longer in use.

A central control room located at the furnace contains a very complete set of Bailey indicating and recording instruments and control devices, with turbo-blower, pulverizers and flue system drafts all being controlled automatically from that point (Fig 5).

The furnace is now treating 20,000 tons of slag per month. Dump slag is mined by a bulldozer and ripper and remelted in the blast furnaces, no cold dump slag being charged direct to the fuming furnace. Molten slag is brought to the converter aisle in 12.5 ton ladles carried on transfer cars. Four ladles, including the shells, constitute a charge. Blowing time varies from 90 to 110 min., depending on rate of slag production at the blast furnaces.

Coal flow to the furnace is controlled by the velocity of primary air passing through the pulverizers. Since back pressure at the tuyeres is 6 lb when the furnace is empty and increases to 11 or 12 lb when it is fully charged, the volume of primary air, measured in terms of free air at sea level, must be constantly increased to maintain the same velocity. When charging starts, coal flow is reduced in order more nearly to complete combustion, the resulting high temperature serving to heat up the slag and smelt the shells. During this period, total air is held at 14,000 cfm and primary air ranges between 5,000 and 6,000 cfm, maintaining a coal flow of 140 lb per min. After the last shell is charged, usually in about 20 min., total air is reduced to 13,000 cfm and primary air increased to 6,500 cfm, raising coal flow to 190 lb per min. Volume of primary air is never allowed to exceed that of the secondary to prevent blow-back of coal into the secondary lines. The best indicator of rate of fuel consumption is the steam flow from the boiler and under charging conditions this is held at 40,000 lb per hr. During the reducing blow it is maintained at 58,000 lb per hr. Gases enter the boiler at a temperature of 2300° and leave the economizer at 590°. Temperature at inlet to U-tubes is 540 and 225° entering the baghouse. Jacket cooling water amounts to 3,700 gpm and absorbs 2 million Btu's per min. or 44 pct of total heat input.

The blast furnace slag now averages 13 pct zinc and de-zinced slag 1.8 pct zinc, which indicates a recovery of 89.2 pct after allowance for shrinkage. Lead is reduced from 0.80 pct in the heads to 0.03 in the tails. Combined fume from the boiler flues, coolers and baghouse weighs 50 lb per cf and has the following analysis:

Zn	Pb	Cu	SiO_2	Fe	As
68.0	6.0	0.25	0.9	0.8	0.20

This fume is deleaded by the process developed at Tooele, which consists of roasting in rotary kilns with a small amount of coke breeze to volatilize lead oxide. From a 300 ton surge bin, the fume is carried by screw conveyor and bucket elevator to a hopper which feeds either or both kilns. 1.0 pct coke breeze is added by screw feeder. The two kilns are 5 ft 6 in. id by 75 in. long, and are fired with natural gas. Temperature is automatically maintained at 2300°F by radiation pyrometers focused on the clinker at the point of discharge. Lead oxide fume is drawn from the kilns through twenty-four U-tubes, by a 20,000 cfm fan and discharged into the lead section of the baghouse. The collected fume, carrying 38 pct Pb and 30 pct Zn is returned to the lead plant. The de-leaded clinker, weighing 150 lb per cf and carrying 76.0 pct Zn and 2.0 pct Pb drops into a Traylor tube cooler, one of which is provided for each kiln, is crushed to pass a ⅜ in. screen, and is loaded into cars for shipment to a retort smelter.

Electrical Resistivity Measurements on Iron-silicon Compacts Prepared by the Powder Metallurgy Procedure

○ ○

FRANK W. GLASER*

Introduction

Iron-silicon alloys have had a great influence, in many ways, in modern industry. Silicon steels have been used almost exclusively for the construction of electrical machinery, but have also become an important material for structures which benefit by the high tensile and yield strengths of this material. In elaborating on the early history of work done on iron-silicon alloys, Greiner, Marsh and Stoughton[1] went back as far as 1808, and pointed to Berzelius as the first producer of ferrosilicon. During the last twenty years some very important contributions in the form of studies of the iron-silicon system, as well as of the physical properties of these alloys, have been published. In consideration of the brittleness and poor machinability of alloys containing more than 5–6 pct Si, commercial interests have stimulated the research done on iron-silicon alloys, but mainly in the range of 0 to 6 pct Si. Yensen[2] has shown the influence of impurities, such as carbon, sulphur and phosphorus on the magnetic properties of 2, 4, and 6 pct Si alloys. Corson[3] extended his investigation of physical properties to approximately 32 pct Si, and attributed the brittleness of the high-silicon material to the particular constitutional features of the alloys. Though mentioned earlier in the literature, the effect of nitrogen on crystal growth and magnetic permeability of iron-silicon alloys has been demonstrated recently by Morrill[4] and Rostoker,[5] respectively. In all the above quoted investigations, except that of Rostoker,[5] sand or chill casting processes were employed for the preparation of samples.

A major advantage of the powder metallurgy process is that it does away with time-consuming machining in many applications. The powder metal industry is always interested in producing a finished product employing a material which has presented considerably greater difficulties in manufacture by other methods. Steinitz[6] described preparation and testing of various Fe-Si alloys which were produced by the powder metallurgy process for the manufacture of armatures for small electric motors or generators. While Steinitz investigated alloys up to 6 pct Si, Rostoker[5] went as high as 9 pct Si. The author[7] previously discussed the diffusion of iron-silicon compacts containing 6 and 10 pct silicon.

It is the object of this paper to study the progress of diffusion occurring in iron-silicon alloys by electrical resistivity measurements. All samples were prepared by pressing and sintering of compacts. Iron, silicon, and Fe-Si powders of various mesh size and compositions were employed to obtain test samples. It was assumed that complete diffusion had been obtained when the electrical resistivity reached a constant value characteristic for that particular alloy. To this end, electrical resistance measurements were used to follow the progress of alloying under various conditions.

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TP 2660 E. Discussion of this paper (2 copies) may be sent to *Transactions* AIME before December 1, 1949. Manuscript received March 11, 1949.

* American Electro Metal Corporation, Yonkers, N. Y.

[1] References are at the end of the paper.

Table 1 . . . Raw Materials Employed

Powder No.	Type	Typical Analysis, Pct								Wt. Loss in H_2
		Fe	Mn	Ni	Cr	C	Al	Ca	Si	
1	Electrolytic iron	bal.				0.004				0.65
2	Fe-Si (85-15)	83.1	0.6	0.3	0.2	0.70	0.3	trace	15.4	
3	Fe-Si (75-25)	74.0				0.03			25.2	
4	Fe-Si (50-50)	bal.	0.4	0.15	0.1	0.04	1–1.2	0.08	49.8	
5	Silicon	0.82				0.10	0.75	0.25	97.6	

The difficulty of microscopic evaluation of the degree of diffusion and of approach to homogenization in Fe-Si alloys was a prime cause for this investigation. Although there have been some important publications during recent years, they have not helped to clarify the rather complex situation occurring in compacts wherein diffusion may be only partial.

Table 2 . . . Densities of Fe-Si Alloys

Pct Si	Values obtained by		
	Bedel*	ASTM[9]	This Investigation
6		7.43	7.46
10	7.1		7.13
25	6.15		6.18
50	4.7		4.68

* Bedel's results were plotted, and the tabulated values were taken from this curve.

Materials, Preparation of Samples and Testing Methods

Table 1 gives data concerning the powders employed for this work. All powders were mixed in appropriate proportions to give the desired overall silicon content, and were subsequently tumbled for one hour.

Samples 2.5 cm × 1 cm × 1 cm were produced by single action hot pressing in graphite dies heated by direct conduction. The hot pressing procedure was chosen in order to avoid compacting difficulties which otherwise occur during cold pressing operations with high silicon-containing powders. Relatively high initial densities were obtained by this method. In certain cases an expansion of samples was observed during the initial subsequent heating period, and was attributed mainly to the evolution of gases, an occurrence frequently encountered in Fe-Si materials. This effect was never large enough to interfere with subsequent and continued densification, although sintering was slowed down to some extent. Pressures employed during hot pressing ranged from 1 to 2 tsi, and the hot-pressing temperature was selected to be below the melting point of the alloy.

Heating was done in a Globar-heated furnace in an atmosphere of either hydrogen or cracked ammonia. Atmosphere purity was controlled to a high degree by the use of drying towers and gettering.

Electrical testing was done with a Kelvin Bridge in which the potential drop for a current of 10 amp was measured over a length of 1.5 cm at room temperature.

In 1932 Bedel[8] published data of experimentally determined densities of cast specimens. The data of Table 2 are as reported by Bedel and have been accepted as a theoretical density basis for all specimens prepared during this investigation. These are in good agreement with results obtained in this investigation. The comparison is given in Table 2.

Homogenization Study of Individual Alloy Compositions

50 PCT SILICON

Samples containing 50 pct silicon were prepared from: (1) silicon powder mixed with electrolytic iron powder (*powders 1 and 5*) and (2) prealloyed 50/50 ferrosilicon (*powder 4*).

Only coarse powders, through 100 mesh, could be employed during the processing of this composition, since all compacts of finer powders could not be prevented from oxidizing during heat treatment.

Samples in group (1), above, which were hot pressed at 1080°C, showed an initial increase of electrical resistivity during the first hours of heat treatment at 1180°C. After reaching a maximum, the resistivity dropped to a constant level after about 8 hr at temperature. This is similar to previously reported behavior for hot-pressed samples.[7] Fig

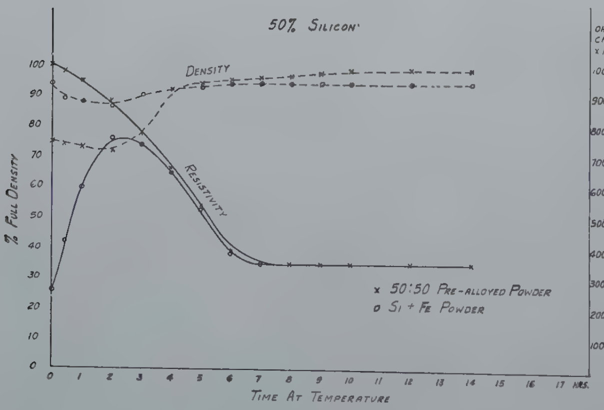

FIG 1—Density and electrical resistivity vs. time at 1180°C after hot pressing. Alloy: 50 pct silicon.

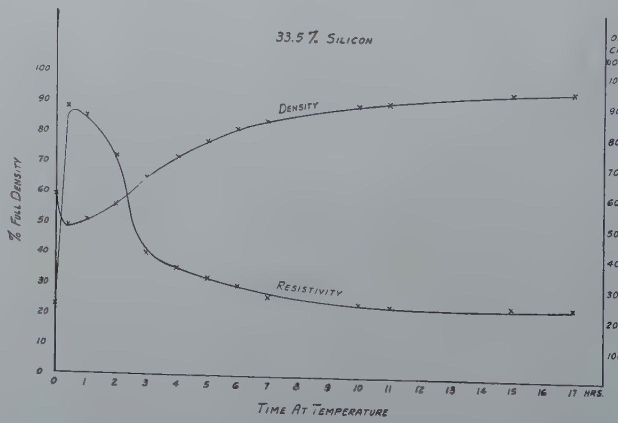

FIG 2—Density and electrical resistivity vs. time at 1180°C after hot pressing. Alloy: 33.5 pct silicon.

1 shows density and electrical resistivity behavior after hot pressing and during the heating cycle. The minimum resistance value in the "as hot pressed" state is far above that of pure iron, and it is therefore believed that some diffusion had already taken place during hot pressing, thereby setting up high silicon grain boundary "barriers" to the current through a "series-resistance" network. The formation of this high resistance skeleton continued with time at temperature and increasing diffusion. After approximately 1 hr and 50 min. at temperature (1180°C), a maximum resistivity was reached for the 50 pct Si material, whereas, as previously reported, only 25 min. were necessary for the 6 and 10 pct Si materials to reach this peak value.[7]

Another possible explanation for this maximum is the formation of an Fe-Si-C phase, since some carbon was introduced during hot pressing through the use of graphite dies, and was still present at this point in the heat treatment. An intergranular phase was visible upon microscopic examination. The microhardness of this phase was much closer to that of an iron-silicon alloy than that of silicon carbide. This seems to favor the first theory. It was found that progressive decarburization of the compacts occurs during heat treatment.

Diffusion seemed to be completed after approximately 8 hr, at which point a resistivity value of 350 microhm-cm was reached. The density was relatively high for this material throughout the heat treatment and seemed to reach a maximum point of densification after only 4 hr of heating.

When prealloyed 50/50 ferrosilicon powder was hot pressed at 1080°C and heat treated at 1180°C, both the density and resistivity showed behavior otherwise encountered only after sintering operations (see Fig 1). Contact resistance showed a gradual decrease as continued solid bonding took place between the particles. As soon as pore space was greatly reduced by densification and the measured cross-section became a true measurement (after approximately 6 hr), the same resistivity of 350 microhm-cm was reached. When this prealloyed material was hot pressed at 1200°C, this resistivity value was reached immediately, and the concomitant density was approximately 100 pct. The use of higher hot pressing temperature thus eliminates approximately 6 to 8 hr of heat treatment.

Table 3 . . . Density and Resistivity of Homogenized Material After Hot Pressing*

Hot Pressing Temp. °C.	Density Pct	Resistivity Microhm-cm
1080	86.0	255
1150	95.5	250
1200	96.0	250

The density of iron-silicon powder mixtures, initially hot pressed at this higher temperature (1200°C), did not differ from that obtained at a lower hot pressing temperature (1080°C). Resistivity, however, was approximately 125 microhn-cm higher at this initial stage, due, presumably, to further progress of diffusion. The curve then followed substantially the aforementioned trend of peak and decrease, reaching complete diffusion at similar time and resistivity values. Samples containing 48.3, 44.1 and 42.2 pct Si, by analysis, were prepared by this same method and showed similar behavior in the relationship between time at temperature and both resistivity and density. Resistivity data for these compositions are reported in a subsequent portion of the text.

33.5 PCT SILICON

This composition was prepared by mixing silicon powder with electrolytic iron powder and hot pressing at 1080°C. Coarse and fine powders behaved alike, and in general it can be said that resistivity and density followed the same general trend as the 50 pct Si alloys throughout the heating period (Fig 2). Only after 10–12 hr was homogenization accomplished. The final resistivity value reached, at complete diffusion, was 235 microhm-cm. This is in agreement with values obtained by Corson[3] for cast materials of similar composition. Some of the completely homogenized material was crushed to powder (through 100 mesh), and re-pressed at various temperatures. Table 3 gives the results for these homogenized materials when hot pressed at various temperatures.

It is obvious from Table 3 that the resistivity is not dependent on the density in this range. Complete diffusion had occurred in all three cases during the prealloying, and the slightly higher resistivity of these samples was attributed to thin grain boundary oxide films which were found to be present during metallographic examinations. The structure of the above three specimens was substantially the same as for samples fully homogenized by heating for 11 hr.

20 TO 27.5 PCT SILICON

A 27.5 pct Si alloy was prepared by mixing a 50/50 Fe/Si master alloy with electrolytic iron powder. The powders (−325 and −100 mesh mixtures) were hot pressed at 1080°C and after a subsequent heat treatment of

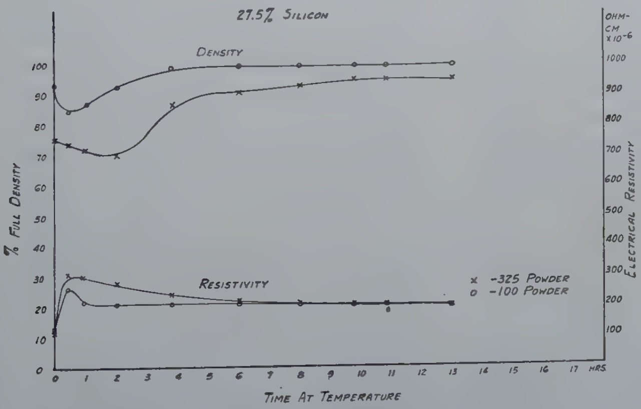

FIG 3—Density and electrical resistivity vs. time at 1180°C after hot pressing. Alloy: 27.5 pct silicon.

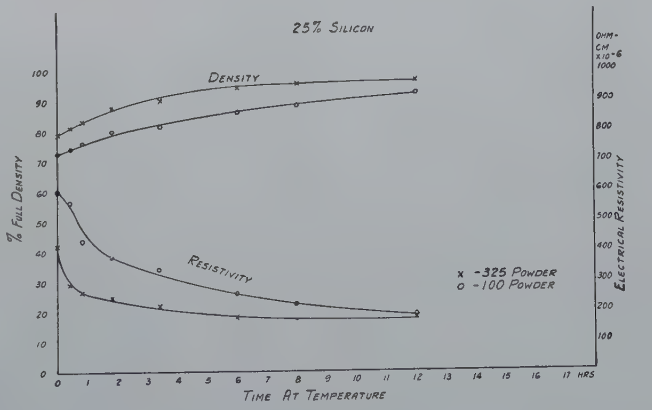

FIG 4—Density and electrical resistivity vs. time at 1180°C after hot pressing. Alloy: 25 pct silicon.

Table 4 . . . Resistivity of Specimens Hot Pressed at 1080°C and Heat Treated at 1180°C

Composition			Resistivity, Microhm-cm			
Alloy Pct Si	Master Alloy	Iron Powder	This Investigation	Corson[3]	Rostoker[5]	Yensen[2]
6	2 and 3	1	85	80	83.5	78
9	2 and 3	1	110	103*	98.6	110†
10.1	2 and 3	1	115	105*		
11.5	3	1	116	98*		
12.5	3	1	60	85*		
13.1	3	1	55	75*		
15.2	3	1	55	40*		
16.6	3	1	62	60*		
18.2	3	1	65	80*		

*Interpolation not too accurate, due to scale of curve.
†Extrapolated.

Table 5 . . . Percent Carbon in Fe-Si Compacts After Various Heat Treatments

Pct Si	Pct Carbon				
	As Hot Pressed	25 Min. at 1180°C	4 Hr	10 Hr	15 Hr
6	0.12	0.10	0.08	0.07	0.04
10.1	0.13	0.04	0.04	0.04	
12.5	0.13	0.03	0.03		

approximately 6 hr at 1180°C a constant resistivity level was reached.

The 25 pct Si alloy was made up by hot pressing a commercial, pre-alloyed 75/25 alloy at 1080°C with a subsequent heat treatment at 1180°C. A state of constant resistivity was obtained after approximately 8 hr of heat treatment for both fine and coarse powders.

The 20 pct Si sample was produced by mixing a 75/25 master alloy with electrolytic iron powder. Only a −325 mesh powder was employed for this composition.

Fig 3, 4 and 5 show the relationship of both the resistivity and density to time at temperature. Trends substantially similar to those observed in previous experiments are noted. Some difference in behavior is noticeable if one considers the particle sizes employed.

For the 27.5 pct Si alloy, the coarse powder follows a rather normal pattern to complete homogenization. The process was slowed down considerably in the case of finer powder because relatively more surface area is exposed to oxidation. This is contrary to the usual alloying process occurring in powders, where the finer powder mixes usually reach equilibrium faster.

Table 6 . . . Fe-Si Alloys Annealed in H_2 and Cracked NH_3 Atmospheres

Approx. Pct Si	Resistivity, Microhm-cm	
	Samples Annealed in H_2	Samples Annealed in Cracked NH_3
6	83.5	85
9	104.5	110
10	111	115
12.5	60	60
20	151.5	152
25	210	205
32	239	235
50	355	350

The 25 pct Fe-Si alloy behaved normally; the finer powder was densified in about half the time required for the coarser powder. Apparently the 50/50 Fe/Si master alloy which was employed in producing the 27.5 pct Si sample had a greater tendency to oxidize than did the 75/25 master alloy.

When fully homogenized 20 pct and 27.5 pct Si alloys were crushed to pass through a 100 mesh and hot pressed at 1080°C, their final resistivity values were obtained immediately on hot pressing. For the commercial, pre-alloyed 75/25 Fe/Si alloy, the hot pressing temperature had to be raised to 1200°C, in order to reach the final resistivity value of this material immediately after hot pressing. When pressed at a lower temperature (1080°C) 8 hr of subsequent heat treatment were needed to attain constant resistivity.

A similar behavior had been noticed with regard to the 50/50 alloy. The precise reason for this difference is not known. Also, the method of manufacture of the commercial material is not known. It is known, however, that the homogenized powders used in this investigation (made by hot pressing and heat treating) were used within a fairly short time after crushing (12 hr max.), and were stored in desiccators even during this interval. Surface oxide film on the commercial powder may account for the increased resistance values found in the hot pressed (1080°C) condition.

6 TO 18 PCT SILICON

All compositions were prepared as shown in Table 4. Testing was done for heat treating times ranging from 25 min. to 17 hr and, with regard to electrical resistivity and density, all materials followed the trends discussed before for other Si alloys. Final resistivity values are also given in Table 4. Some values found in the literature have been entered in the table for comparison.

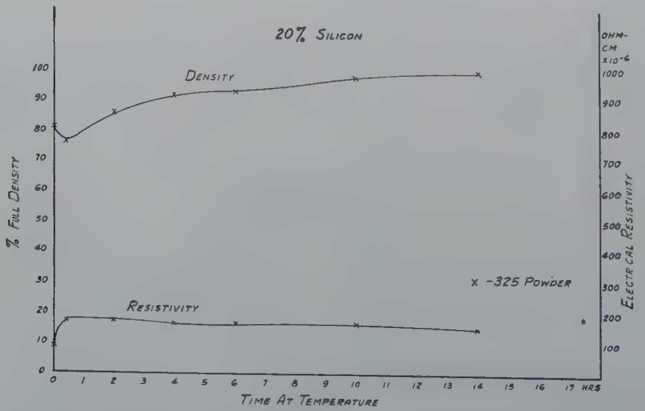

FIG 5—Density and electrical resistivity vs. time at 1180°C after hot pressing. Alloy: 20 pct silicon.

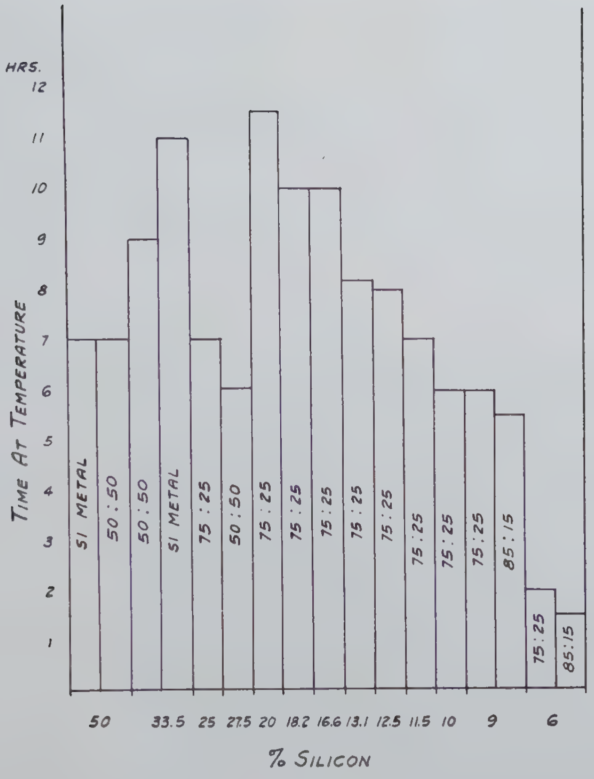

FIG 6—Time needed for complete diffusion for iron-silicon samples prepared from different master alloys. Hot pressing temperature 1080°C. Subsequent heat treatment at 1180°C.

Table 7 . . . Resistivity Values for Fe-Si Alloys After Complete Diffusion

Pct Si (by analysis)	Resistivity (microhm-cm)	Pct Si (by analysis)	Resistivity (microhm-cm)
6.0	85	20.1	152
9.0	110	25.2, 25	182, 180.5
10.1	115	27.6	200
11.5	116	33.5	240
12.5	60	42.2	303
13.1	55	44.1	320
15.2	55	48.3	340
16.6	62	49.8	350
18.2	65		

Fig 6 indicates the time needed for different samples to reach complete diffusion. It is interesting to note that when master alloys are sintered by themselves, both the 50/50 and the 75/25 require the same time (7 hr at 1180°C) to reach constant resistivity.

For a given alloy mixture, 85/15 master alloy requires a somewhat shorter time at temperature, as compared with 75/25, to reach constant resistivity. Also, the less iron added to the 75/25 mixtures (approaching the composition of the master alloy), the longer the time required for equilibrium. If not hot pressed, much longer times at temperature than those reported in Fig 6 are necessary to obtain complete diffusion in iron-silicon materials produced by powder metallurgy processes. Hot pressing temperatures were controlled optically and it is probable that the indicated temperatures were no more precise than plus or minus 20–30°C. Considering the fact that a few degrees C in this temperature range, which is quite critical for these Fe-Si materials, will influence the speed of diffusion considerably, the times reported in Fig 6 represent approximate values.

Carbon analyses have been run for some materials containing 6, 10.1 and 12.5 pct Si, and the results are tabulated in Table 5.

Inasmuch as the original raw material contained less than 0.03 pct C, the C picked up during hot pressing seems to be as high as 0.09 to 0.10 pct.

Metallographic examination disclosed substantial surface carburization of the compacts, and certainly a good portion of both the increased carbon found on hot pressing and the loss of carbon observed after heat treating can be attributed to the carburization and subsequent decarburization going on in the skin of the compact during its cycle.

A comparison has also been made for resistivities obtained with samples annealed in H_2 vs. samples annealed in cracked ammonia. Table 6 shows that the nitrogen contained in this latter atmosphere does not seem to have much influence on the electrical resistivities of Fe-Si alloys.

A characteristic trend of minimum, maximum and constant resistivity level was established as a function of diffusion time for iron-silicon samples prepared from powder mixes.

At the minimum resistivity (the "as hot pressed" stage), diffusion of the silicon into the iron was far from complete, but a certain amount of bonding between particles had taken place. The current passed through a low resistance network. After a given time interval at temperature, diffusion created a high resistance silicon-iron network, accounting for the maximum resistivity. Diffusion, progressing with time, reduced the resistivity to a constant level. If a given ferrosilicon composition was prealloyed by the hot pressing and heat treating procedure, and subsequently crushed to −100 mesh, final resistivity was obtained immediately on hot pressing at 1080°C.

Hot pressing temperatures, higher by 120°C, were required for commercial prealloyed powders to obtain final resistivity immediately upon hot pressing. Grain boundary oxide films are believed to be the cause for the necessity of this higher hot pressing temperature. If a commercial, prealloyed, powder was hot pressed at normal hot pressing temperature, 8 hr of subsequent sintering time was needed to arrive at final resistivity values.

General Discussion of Results

Table 7 shows the resistivity values the author measured for various Fe-Si alloys after complete diffusion. Data as given by Corson[3] have been plotted together with these values in Fig 7.

Distinct differences between the values obtained in these two investigations, especially in the 20–30 pct Si ranges, can be noticed in Fig 7. The present values are generally higher than those reported by Corson, whose specimens were prepared by casting. A comparison of grain size of the alloys employed during the respective investigations disclosed striking similarities. Since no comparisons with regard to chemical purity can be made it can only be pointed out that all Si percentages employed in this investigation have been carefully checked by chemical analysis, and tests have frequently been repeated to minimize any source of error. It will also be recalled that while the samples for the author's experiments have been produced by several methods, the final test results have never varied more than 3 to 5 pct.

All samples were tested for hardness, and Fig 8 shows the relationship of Rockwell hardness vs. silicon content for the fully homogenized samples. Hardness values in Fig 8 are higher for the higher silicon ranges than the values reported by Corson. There may be some relationship between the higher hardness and the higher resistivities as reported in Fig 7.

Metallographic examination of specimens in the 11–25 pct region suggest no cause for the shape of curves for hardness and resistivity. One explanation, recorded by Hansen,[10] was the presence of an order-disorder transformation. An X ray diffraction study of 12.5 pct and 16.6 pct Si alloys showed the presence of lines which were absent in a 10.1 pct Si alloy. These lines corresponded to the calculated positions of the 111 and 200 reflection, and thus are taken to indicate the existence of an ordered state. In this connection it might be of interest to note that some heat treatment experiments have been made with a 15.2 pct Si-containing material. One specimen was kept at 1180°C for 72 hr and cooled to room temperature over a period of approximately 5 hr, while another specimen was quenched in water after this prolonged time at temperature. In both cases the resistivity values as reported for this composition in Fig 7 were still found and no marked difference in structure between these two specimens could be found upon metallographic examination.

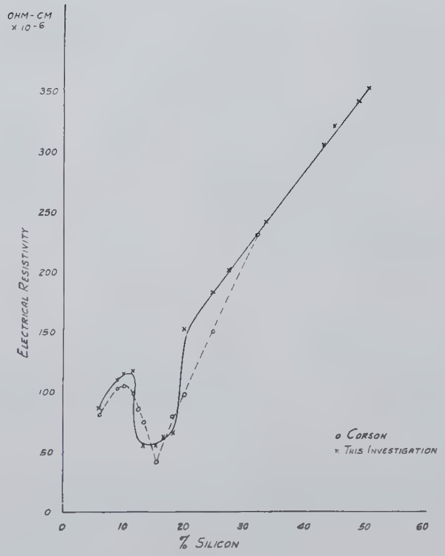

FIG 7—Electrical resistivity vs silicon content for fully homogenized samples.

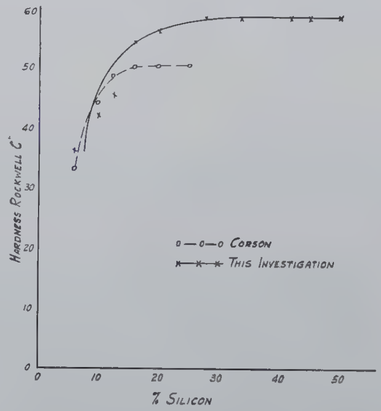

FIG 8—Hardness vs silicon content for fully homogenized samples.

Summary

1. It has been shown that the degree of diffusion in iron-silicon alloys prepared by the powder metallurgy process can be followed by electrical resistivity measurements. In the higher density ranges, the electrical resistivity is a function only of the diffusion process and is very much influenced by changes of the Si concentration in a nonhomogeneous Fe-Si alloy.

2. Values for the specific electrical resistivity of iron-silicon alloys containing between 6 and 50 pct silicon have been determined.

3. It has been further shown that the hot pressing and heat treating process can be used to produce iron-silicon materials in suitable forms.

4. No major effects upon the electrical resistivity of an atmosphere containing nitrogen were detected for iron-silicon alloys.

5. The resistivity curve shows a break between approximately 11 and 25 pct Si.

Acknowledgment

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The writer also wishes to express his gratitude to Messrs. W. Ivanick, R. Steinitz, S. J. Sindeband and R. Wachtell, for their advice and assistance in the preparation of this paper, as well as to Professor J. T. Norton for his cooperation in carrying out the X ray diffraction study.

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A Metallographic Description of Fracture in Impact Specimens of a Structural Steel

M. BAEYERTZ,* Member AIME, W. F. CRAIG, JR.* and E S. BUMPS*

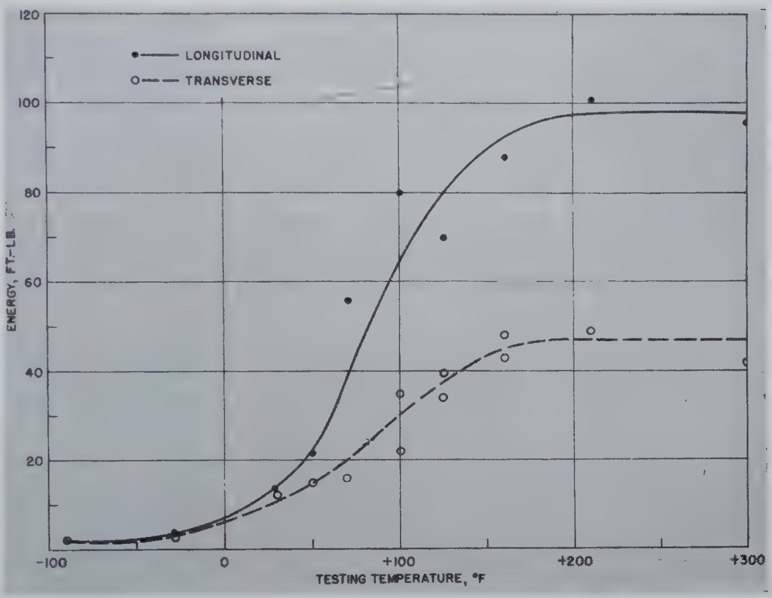

FIG 1—Relation of energy to testing temperature obtained from V-notch Charpy specimens from an ordinary structural steel shape.

Metallurgists have looked at fractures macroscopically for many years and have evolved a vocabulary in which such words as "cleavage," "brittle," "shear," "ductile," "granular," "fibrous," and "silky" are used to describe the appearance of the fractured surface; but the meaning of these words in terms of metal structure is not well established. Observations of the structural meaning of "brittle" and "ductile" fractures in plate steels have been made, notably, by Kramer and coworkers[1] and by Tipper.[2] Grossman[3] has studied the fracture of tempered martensite and combinations of ferrite and martensite. Notwithstanding these and other less concerted attacks on the problem, present understanding of fracture rests more on assumptions and logic than on experiment. It is the purpose of this paper to add a little to the growing fund of experimental observations of the nature of fractures in steel. The particular fractures to be described were obtained in conventional impact testing of an ordinary structural steel shape.

In impact tests of the Charpy type, the specimens fail in a characteristic manner that depends on the steel and the temperature of testing. With ordinary structural and many other steel products, an appropriate range of testing temperature will cause a considerable change in the energy absorbed before fracture. This change is known as the energy transition and is accompanied, more or less closely, by alteration in the appearance of the fracture. At testing temperatures below the transition, the terms "brittle," "cleavage," or "granular" are used to describe the fracture; above it, "ductile" or "shear" are often used. Within the transition, the fracture changes from "brittle" to "ductile" by a progression in appearance, wherein the "brittle" portion of the fracture becomes restricted to a smaller and smaller central area of the fracture, as the testing temperature is raised and the "ductile" type of fracture is approached. All this is well known to metallurgists.

The specimens under consideration are of the conventional V-notch Charpy type. They were taken from a structural steel shape of the following analysis:

C	Mn	P	S	Si
0.17	0.46	0.009	0.029	0.03

Both longitudinal and transverse specimens were tested and examined. Fig 1 shows the energy values plotted against testing temperatures in the usual way. The curves for both longitudinal and transverse specimens show an energy transition, although the maximum energy absorbed at testing temperatures above the transition is greater in the case of the longitudinal specimens.

Fig 2 illustrates the changes in the macroscopic appearance of the fractures that are associated with the energy transitions shown in Fig 1. Macrographs of the fractured surfaces of the specimens have been identified with the fracture ratings at intervals on each fracture curve. The numerical fracture rating on the ordinate of Fig 2 indicates the percentage of the area of each fracture that was considered to be "brittle" on macroscopic observation. Such rating of the fracture type in impact tests is now customary in many laboratories. Hereafter the specimens will be identified by reference to Fig 2 as 90 pct "brittle," 80 pct "brittle," and so on, in accordance with this macroscopic evaluation of the appearance of the fractured surface.

The discussion of the fractures is divided into three parts. The first two are concerned with the mode of fracture and its relation to general structural features. As the same metallographic features occur in both longi-

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* Armour Research Foundation of Illinois Institute of Technology.

[1] References are at the end of the paper.

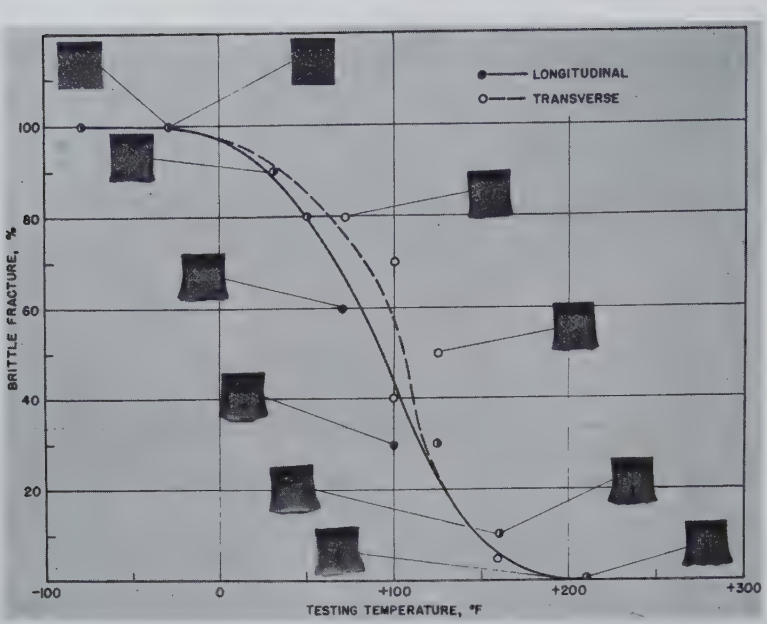


FIG 2—Relation of type of fracture to testing temperature obtained from V-notch Charpy specimens from an ordinary structural steel shape.
Corresponding energy curves are shown in Fig 1.

tudinal and transverse fractures, differing in degree and distribution but not in kind, the illustrations and description are drawn from both types of specimens. The third part of the discussion deals with some relations between the structural features of fracture and the energy values obtained in the test. In this part the relation between longitudinal and transverse data will be discussed.

Character of the Fractured Surface

Leaving aside for the moment consideration of "ductile" fracture, the most prominent feature of the fractured surfaces in Fig 2 is the group of shiny facets to be seen on the "brittle" regions. These facets look alike and are of about the same size regardless of testing temperature, as

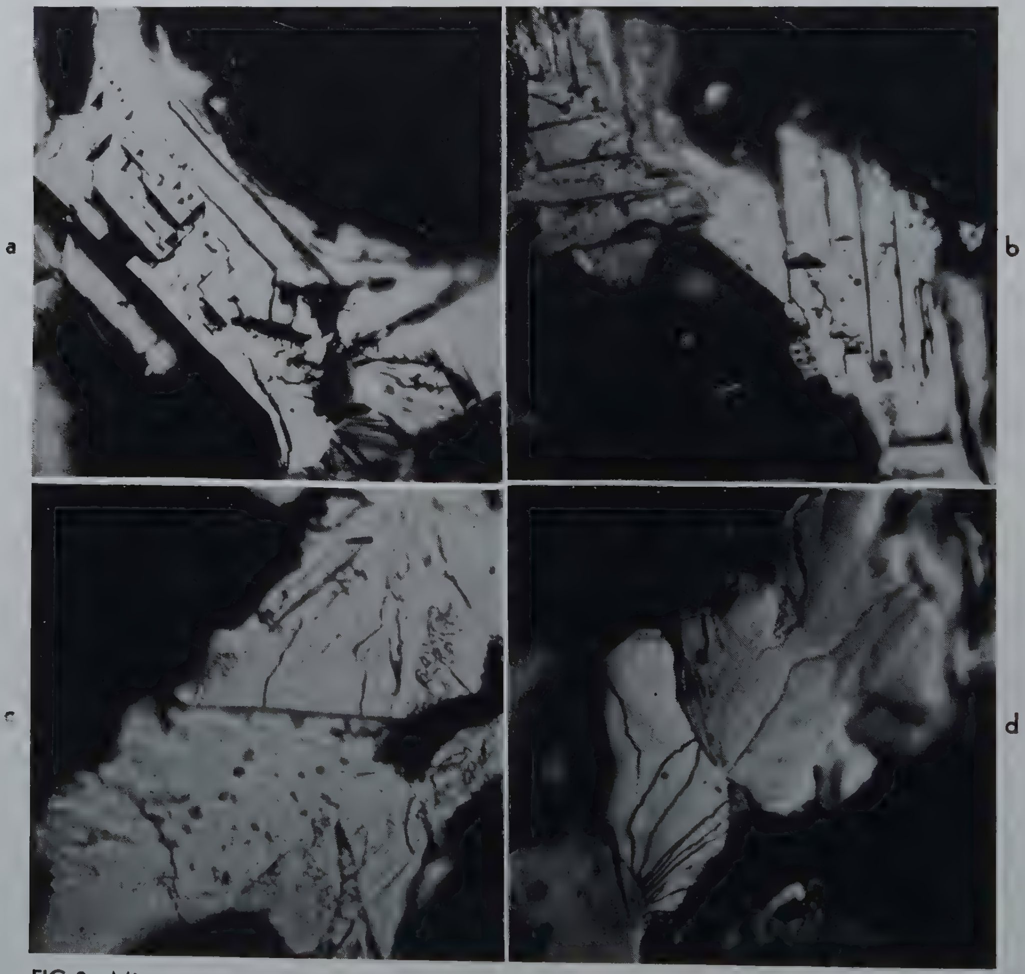
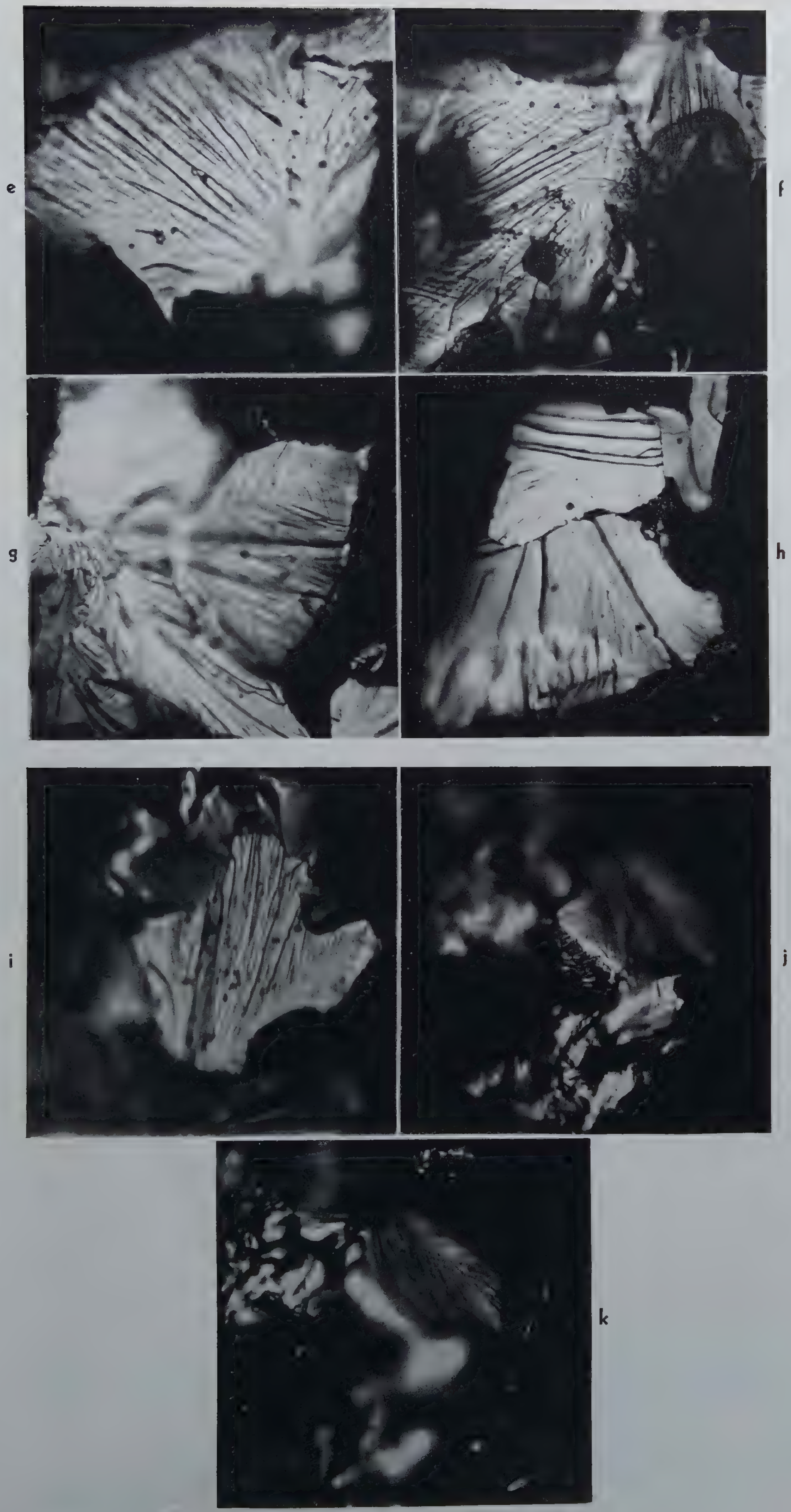


FIG 3—Microscopic appearance of cleavage facets on fractured surfaces of impact specimens. Series covers transition range from 100 pct "brittle" fracture to 100 pct ductile fracture.
a—100 pct "brittle" fracture. 750 ×
b—90 pct "brittle" fracture. 750 ×
c—80 pct "brittle" fracture. 750 ×
d—60 pct "brittle" fracture. 750 ×
e—60 pct "brittle" fracture. 750 ×
f—30 pct "brittle" fracture. 750 ×
g—10 pct "brittle" fracture. 750 ×
h—10 pct "brittle" fracture. 750 ×
i—5 pct "brittle" fracture. 750 ×
j—0 pct "brittle" fracture or 100 pct "ductile" fracture. (Same as Fig 3 k but focused at slightly lower plane. 750 ×
k—0 pct "brittle" fracture or 100 pct ductile fracture. (Same as Fig 3j but focused at slightly higher plane.) 750 ×
All micrographs slightly reduced in reproduction.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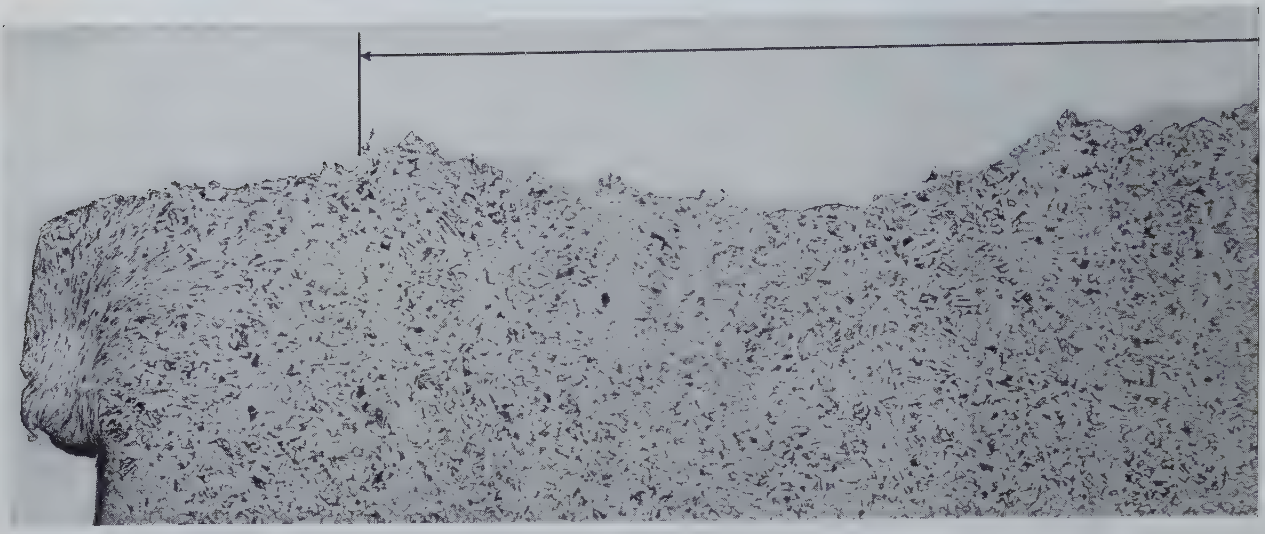


FIG 4—Section through 90 pct "brittle" fracture. "Brittle" portion of fracture is enclosed by bracket.
50 ×. Etchant 2 pct nital. Reduced approximately one fourth in reproduction.

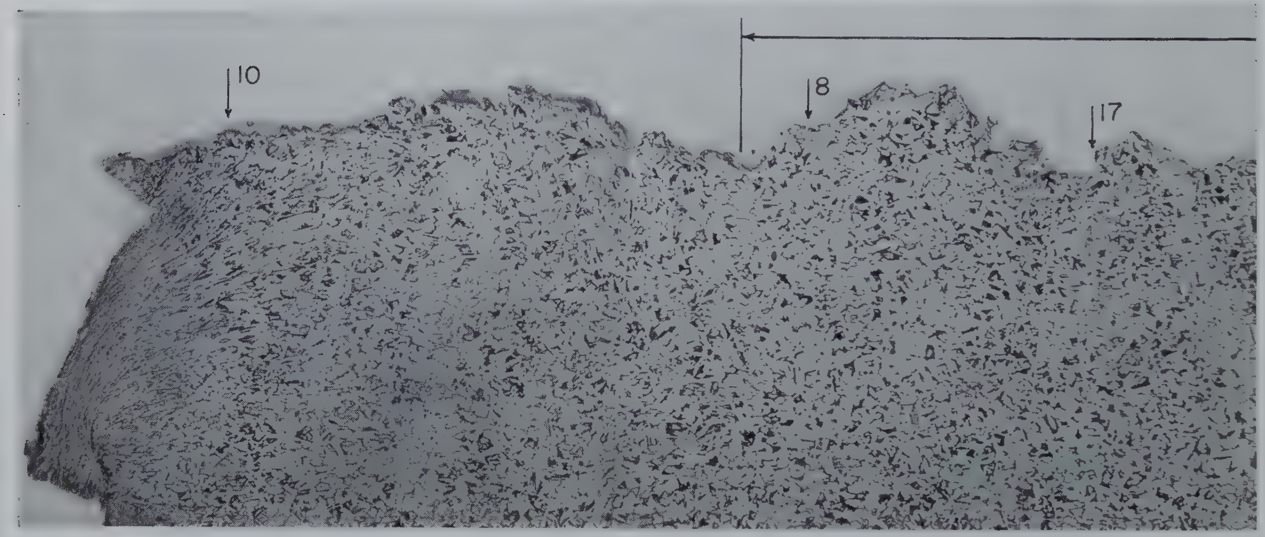
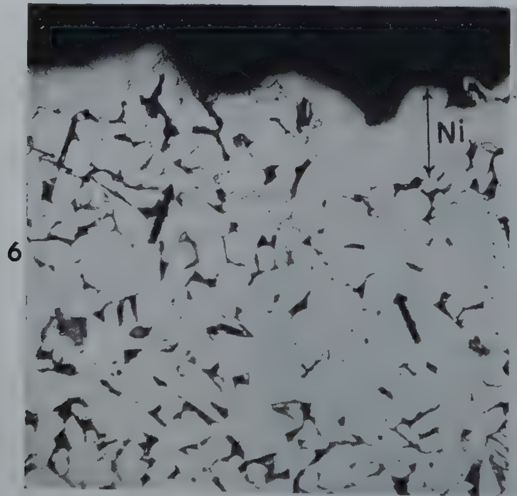


FIG 5—Section through 60 pct "brittle" fracture.
"Brittle" portion of fracture is enclosed with bracket. Arrows indicate figure numbers of micrographs showing detail. 50 ×. Etchant 2 pct nital. Reduced approximately one fourth in reproduction.



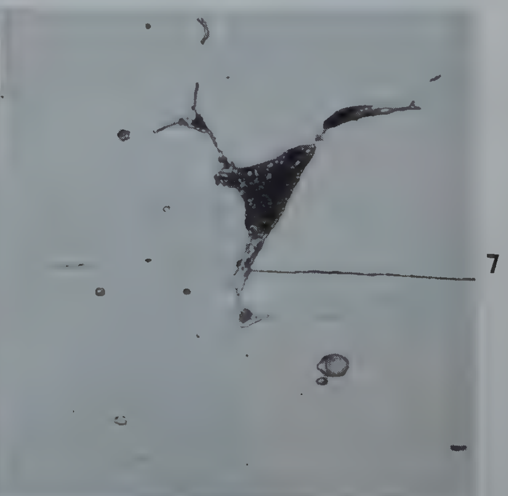


FIG 6 (left)—Portion of "brittle" region of 30 pct "brittle" fracture.
Single arrows indicate ferrite cleavages below the path of main fracture. 150 ×. Etchant 2 pct nital.

FIG 7 (right)—Detail of cleavages in the two ferrite grains indicated by the arrow on the right of Fig 6.
Note that the cleavage was apparently interrupted by the pearlite colony. 1000 ×. Etchant 2 pct nital. Both micrographs slightly reduced in reproduction.

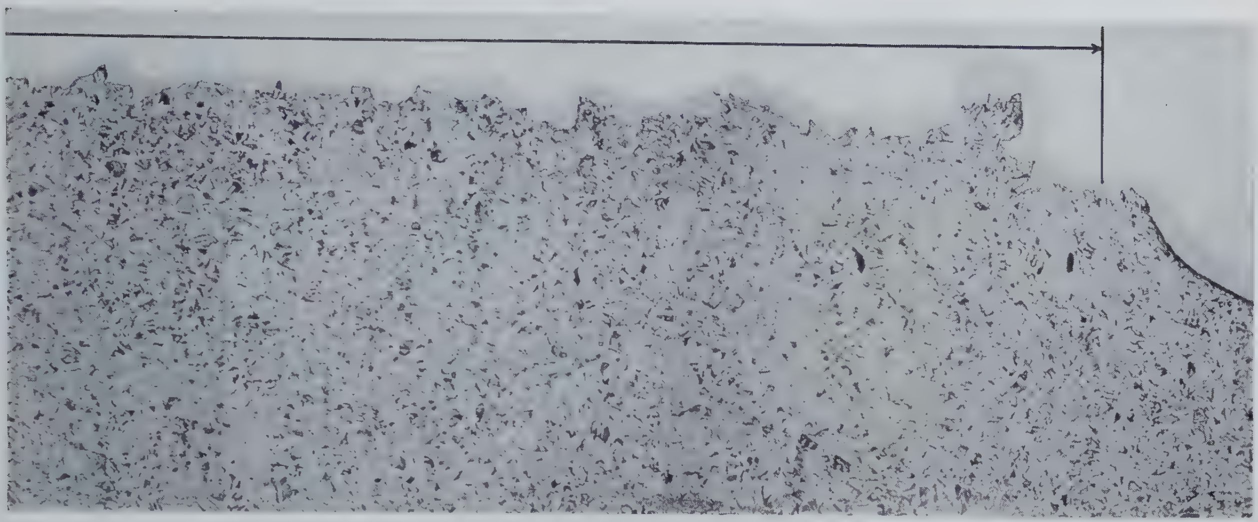


Fig 4—(Continued)

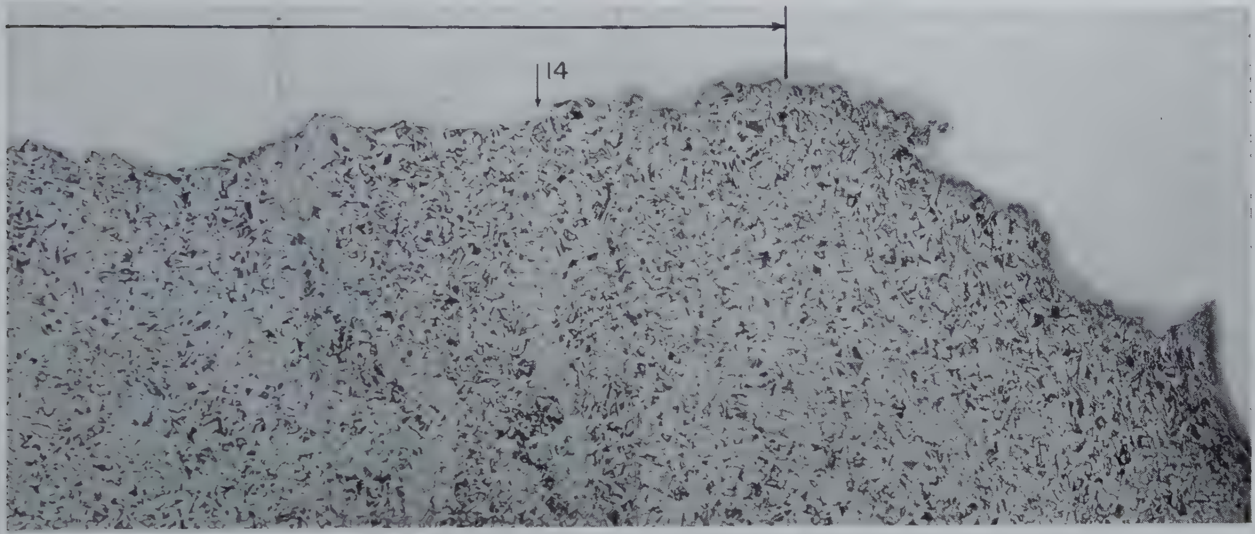


Fig 5—(Continued)

long as they appear at all. This suggests a relation to the structure of the steel.

On raising the magnification, but still looking toward the fractured surface, the facets have the appearance illustrated by Fig 3. It now becomes apparent that the facets are not alike, as they seemed at lower magnification. Instead, straight cleavage planes characterize the low temperature end of the transition range, while definite and then pronounced evidence of deformation is observed on the cleavage facets as the high temperature end of the transition range is approached. "Cleavage" as used here and in the rest of the paper is crystallographic cleavage, not the loose application of the term to describe the macroscopic appearance of the fracture.

At low testing temperatures, represented by the specimens with 100 pct and 90 pct "brittle" fractures, the cleavage planes are flat and resemble the cleavage facets of ferrite described by Zapffe and Moore[4] and by Kramer and coworkers.[2] The cleavage planes make well defined angles with each other that appear to be the 90° angles to be expected from the {100} cleavage observed in ferrite by Barrett, Ansel and Mehl.[5] Tipper[2] has found that the {100} cleavage is that shown by the ferrite in ship plate fractures.

As the testing temperature is raised, the tendency for multiple cleavage on several of the {100} family appears to diminish, giving rise to the larger, comparatively smooth facets shown by the 80 pct "brittle" fracture. Also there is another change in the character of the fracture. Small ripples appear on the cleavage surfaces. These ripples are believed to be caused by cold work, either prior to or at the time of cleavage. It is difficult to distinguish between prior and concurrent cold work, but the complexity of slip directions to be seen as the testing temperature is raised suggests that at least a part of the slip occurs in the ferrite before cleavage takes place. A part of the rippling may be caused by the stress waves set up by the operation of cleavage.

Multiple slip in three directions on single cleavage facets may be seen in the micrographs of the 30 pct and 10 pct "brittle" fractures. The extent of such slip probably is related to the orientation of the ferrite grain with respect to the stress pattern. Two micrographs are included in Fig 3 for the 60 pct and 10 pct "brittle" fractures. Each pair of photographs shows qualitatively the range in the amount of slip observed on the various cleavages of the fracture.

The final micrographs in the series in Fig 3 illustrate the highly distorted cleavage planes observed in the 0 pct "brittle" fracture obtained with a testing temperature of 210°F. Macroscopically this fracture appeared to be 100 pct "ductile," as may be seen in Fig 2. Microscopically the same sort of cleavage facets are to be seen in the central region of this "ductile" fracture as were observed on the "brittle" regions of the other fractures, with the exception that the cleavage facets of the "ductile" fracture are so rumpled by cold work that they do not reflect enough light to be detected macroscopically as cleavage facets. Thus, under the triaxial loading in an impact specimen during testing, "ductile" fracture appears to be initiated by ferrite cleavage in essentially the same way as in the more "brittle" fractures that are obtained at lower testing temperatures.

The Mode of Fractures

Turning from examination of the fractured surface to the metal below the surface, even more light is shed on the mode of impact fracture in ordinary structural steel. For this part of the study, the fractured specimens were plated with nickel, sectioned and prepared for metallographic examination. In each specimen the section studied lay on a plane that was normal to the fractured surface and extended from the notch to the back of the specimen.

Fig 4 and 5 are illustrations of the structural features observed in the metal below the "brittle" and "ductile" portions of fractures. Fig 4 shows a section normal to a 90 pct "brittle" fracture. The portion on which the ferrite cleavages were observed is included by the bracket. Similarly, Fig 5 shows a section normal to a 60 pct "brittle" fracture. The thickness of the specimen after fracture (distance between the notch and the back of the specimen) indicated the greater reduction before final rupture in the specimen having the 60 pct "brittle" fracture. In Fig 5, the region of ferrite cleavage is restricted and cold work, especially at the notch, has become more apparent than in the 90 pct "brittle" specimen in Fig 4. For the purpose of orienting the reader, the figure numbers of photographs at higher magnification to be described below have been placed in their respective positions along the fracture in Fig 5.

On examination of the metallographic sections at higher magnifications, the mode of development of the fracture becomes evident. With the exception of shock twinning at low testing temperatures, to be discussed later, the essential details of cleavage, deformation and fracture did not vary throughout the transition range, although these features apparently differed in amount with change in testing temperature. Because of this similarity in the mode of cleavage, deformation and fracture, illustrations will be drawn from several of the specimens broken within the transition.

The metallographic evidence supports the following sequence of events leading to the final rupture of the specimens. As the hammer of the impact testing machine strikes the specimen and bends it, elastic and then plastic deformation occurs. Within the general region of greatest triaxiality of loading located somewhat back of the notch in the specimen, the restraint to deformation and the nature and temperature of the steel are such as to cause cleavage within the ferrite grains when the tensile stress normal to a cleavage plane reaches an appropriate value. The ferrite cleavage may occur either within the elastic or the plastic portion of deformation depending upon the testing temperature. The cleavage occurs only in grains or groups of grains whose cleavage planes are favorably oriented with respect to the stress pattern. Such cleavage involving two ferrite grains is indicated by the arrow on the right side of Fig 6, and is shown at higher magnification in Fig 7. Other similar cleavages are shown in Fig 8. In the fractured specimens, such cleavages were observed only in the immediate vicinity of the fracture.

As described previously and illustrated by Fig 3, cleavage at the low temperature end of the transition apparently occurs before the yield point is reached. At the high temperature end of the transition, there is evidence of cold work preceding cleavage. Intermediate stages between these two extremes occur within the transition range. Evidence of deformation before cleavage at the high temperature end of the transition is to be seen also in the samples prepared for metallographic study. Fig 9 shows cleavage involving three ferrite grains in a 10 pct "brittle" specimen. The bent cleavage on the right side of the micrograph is taken as an indication of cold work before cleavage. Deformation after cleavage would be expected to separate the two surfaces of the cleavage in the manner illustrated by the cleavage at the fracture surface in Fig 8.

To continue with the events preceding final rupture, the greater the extent of cleavage the less will be the effective section of the metal left to withstand subsequent loading during the test. Also the stress pattern will be altered, because each cleavage will now have become an internal notch. In the next stage the metal between the cleavages, and that in the peripheral regions of low triaxiality of

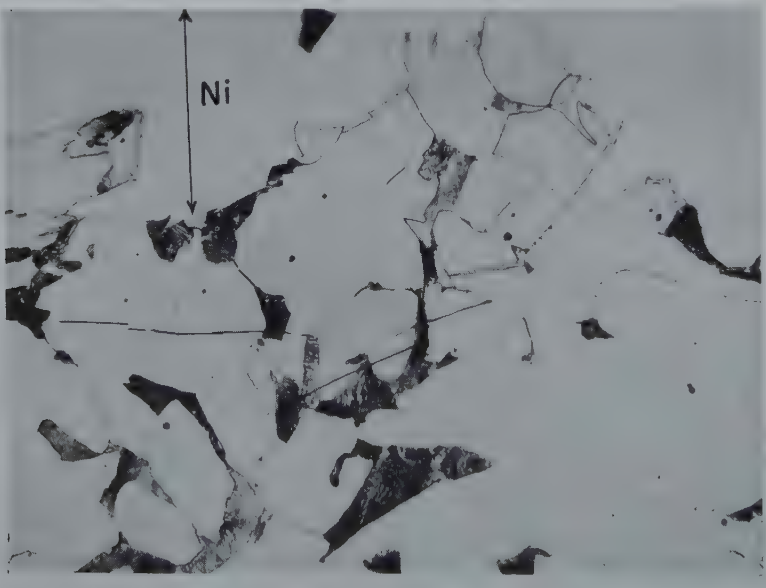


FIG 8—Cleavages observed in the "brittle" portion of the 60 pct "brittle" fracture. 500 ×. Etchant 2 pct nital.

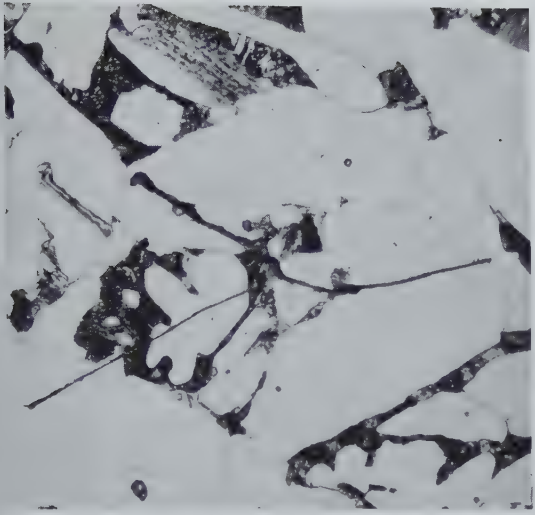


FIG 9—Cleavages in three ferrite grains in a 10 pct "brittle" fracture.

The bent cleavage on the right side of the micrograph indicates plastic deformation before cleavage. 500 ×. Etchant 2 pct nital.

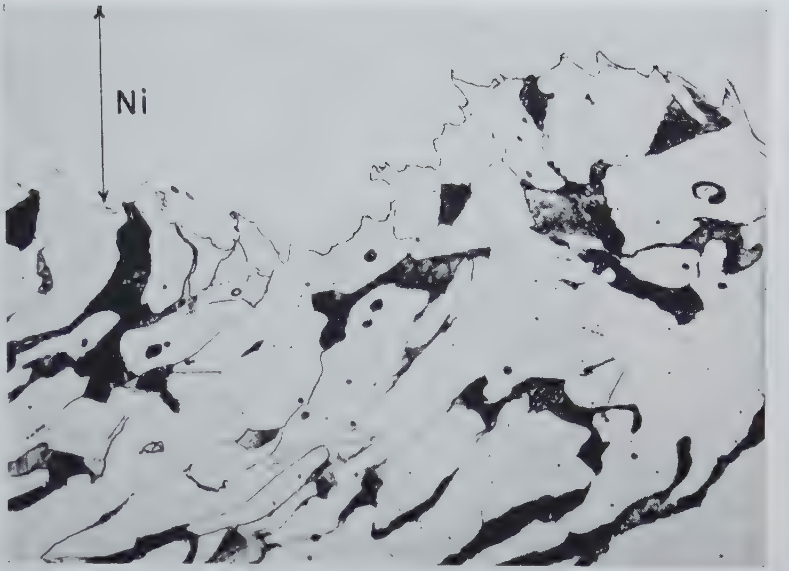


FIG 10—Evidence of deformation in the peripheral "ductile" region of a 60 pct "brittle" fracture.

500 ×. Etchant 2 pct nital.

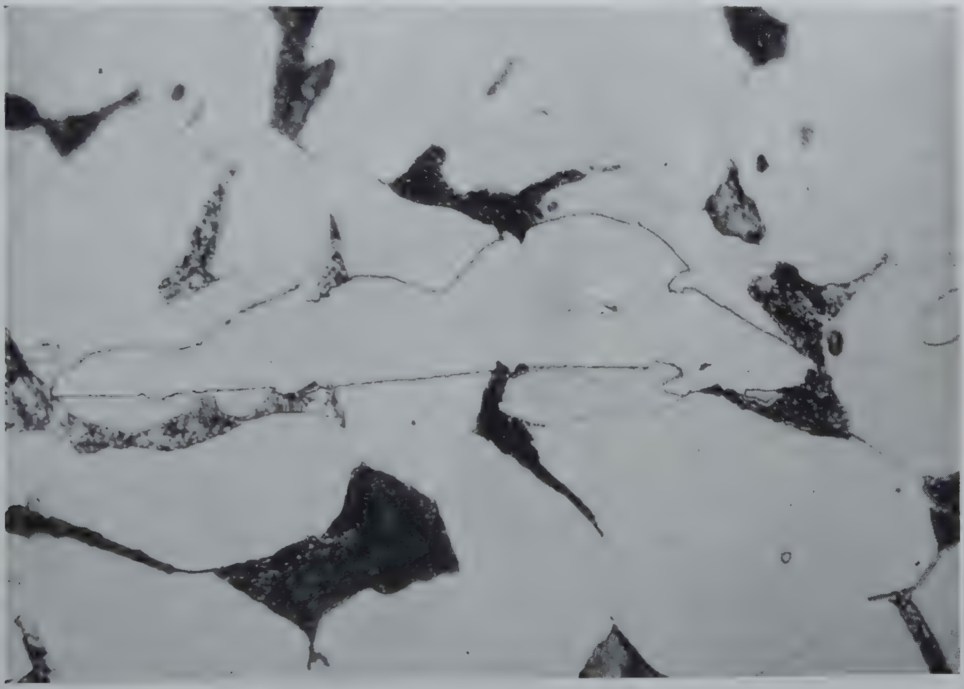


FIG 11—Detail of the nickel filled crack indicated by the arrow on the left of Fig 6.

Two colonies of pearlite were pulled apart. 1000 ×. Etchant 2 pct nital.

stressing, deform and fracture. Evidences of deformation in the peripheral "ductile" region have been illustrated already in Fig 2, 4 and 5. Microscopically, the fracture of such regions is illustrated by Fig 10.

In the central "brittle" region, one feature of the deformation after the cleavage is the pulling apart of cleavages formed earlier. Numerous cleavages are formed in the general region of the final rupture, but only a limited number form a part of the path of ultimate rupture. Some of the cleavages remain intact as indicated by the arrow on the right side of Fig 6 and in Fig 7. Others are pulled apart as indicated by the arrow on the left side of Fig 6. This crack was filled with nickel when the specimen was plated. It may be seen in more detail in Fig 11. The upper surface of the cleavage has pulled away from the lower surface, and in so doing, has broken apart two colonies of pearlite. Similar pulling apart of cleavages may be seen in Fig 8. Fig 12 shows an instance in which stepwise slip occurred on the upper half of the cleavage during deformation subsequent to cleavage but preceding final rupture. Apparently ferrite grain boundaries constitute a weak region where the cleavage extends through adjacent grains, as illustrated by Fig 13.

When more than one cleavage occurs in a ferrite grain, as on the left of Fig 8, the final path of fracture may include the several cleavages. In such a case the final rupture occurs by tearing between the cleavages, as indicated in Fig 14. The arrows indicate the torn edges.

In the absence of experimental observations, there has been an inclination

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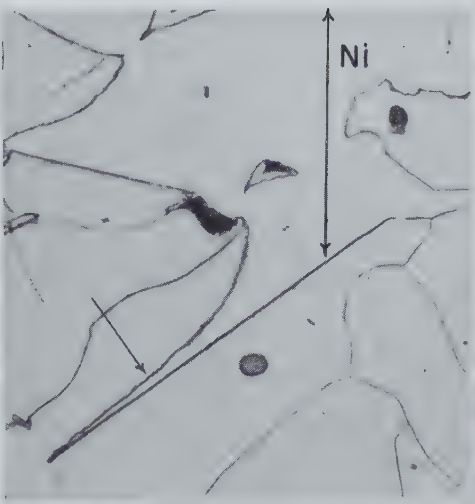

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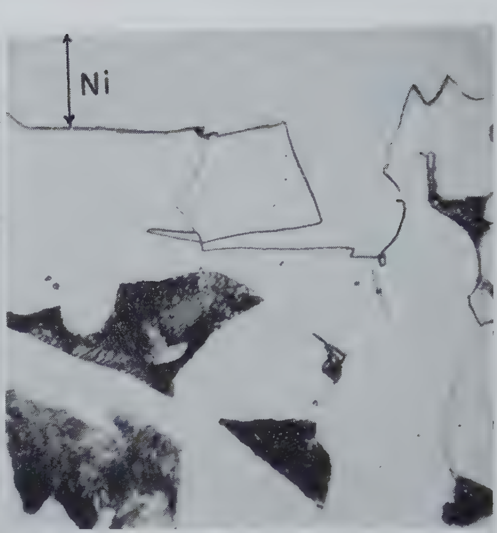

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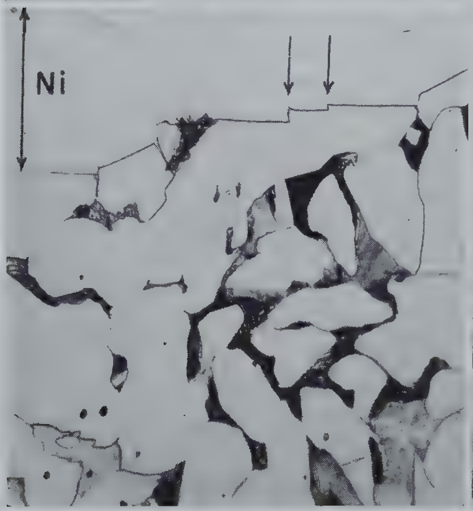

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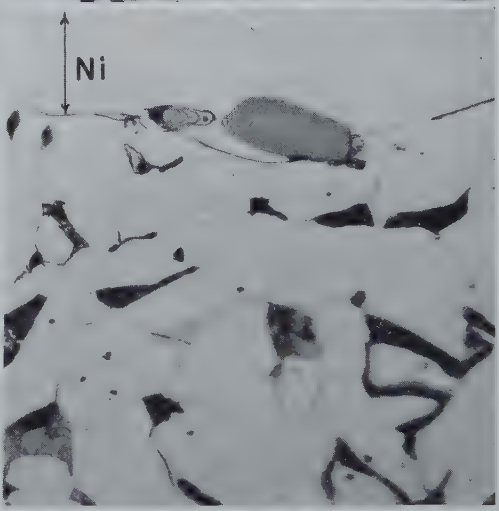


FIG 12—Evidence of stepwise slip that preceded final rupture in a 60 pct "brittle" fracture.
1200 ×. Etchant 2 pct nital.

FIG 13—A 90 pct "brittle" fracture.
Cleavage in adjacent ferrite grains is joined by fracture along a grain boundary. 1000 ×. Etchant 2 pct nital.

FIG 14—Example of tearing between cleavages as observed in a 30 pct "brittle" fracture.
500 ×. Etchant 2 pct nital.

FIG 15—A (Mn, Fe)S inclusion adhering to a torn region of the fracture of an 80 pct "brittle" fracture.
500 ×. Etchant 2 pct nital. Micrographs slightly reduced in reproduction.

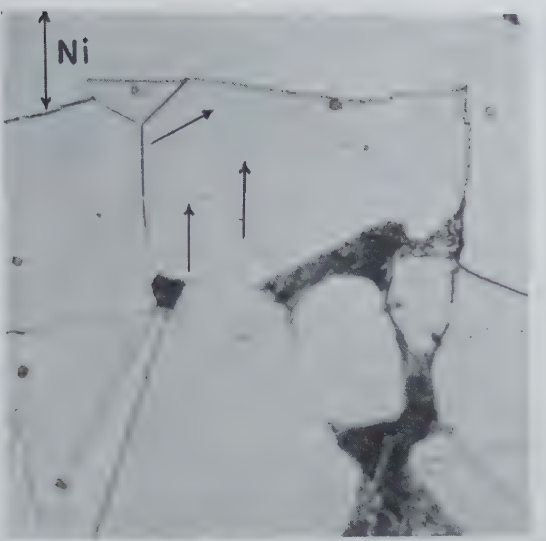
on the part of some metallurgists to blame the initiation of "brittle" fracture on phases of little ductility such as carbides or nonmetallic inclusions. No evidence of this has been obtained in this study. On the contrary, the evidence suggests that the cleavage of ferrite initiates "brittle" fracture. To support this viewpoint are the observations of intact pearlite colonies, as in Fig 7 where the cleavage has involved ferrite grains on both sides of the pearlite colony.

There were far fewer inclusions than pearlite colonies in the steel, so that the opportunity to observe their role was limited; however, none of the observed ferrite cleavages could be definitely attributed to inclusions. The inclusions were as apt to be present in the torn regions between the cleavages as near the cleavages. Fig 15 shows a (Mn,Fe)S inclusion still adhering to a torn region of the fracture. While the evidence presented here does not prove conclusively that cementite or inclusions do not initiate the cleavage, yet it seems sufficient to cast doubt on this explanation as the primary cause of the cleaving of ferrite in the impact test. More experimental observations are needed.

Shock twins occurred frequently near the fracture in specimens broken at the low temperature end of the transition, and grew infrequent and then practically disappeared as the testing temperature was raised. Thus a greater proportion of energy went into the formation of twins at the lower than at the higher testing temperatures. Typical shock twins are indicated by the arrows in Fig 16. There was no evidence that the observed ferrite cleavage follows the plane of shock twinning. This was to be anticipated from the work of others[4] who have reported that the twinning and cleavage planes in ferrite are {112} and {100} respectively. The lack of coincidence is illustrated by Fig 16 in which the shock twins and a cleavage facet occur at a slight but definite angle with respect to each other. If the cleavage had resulted from weakness of lattice registry along the interface between the shock twin and the parent ferrite grain, one would not expect the structure shown in Fig 16.

Dependence of Transverse and Longitudinal Energy Values on Structure

This portion of the discussion is based on more limited observations than the foregoing description of the mode of fracture; however, it seems



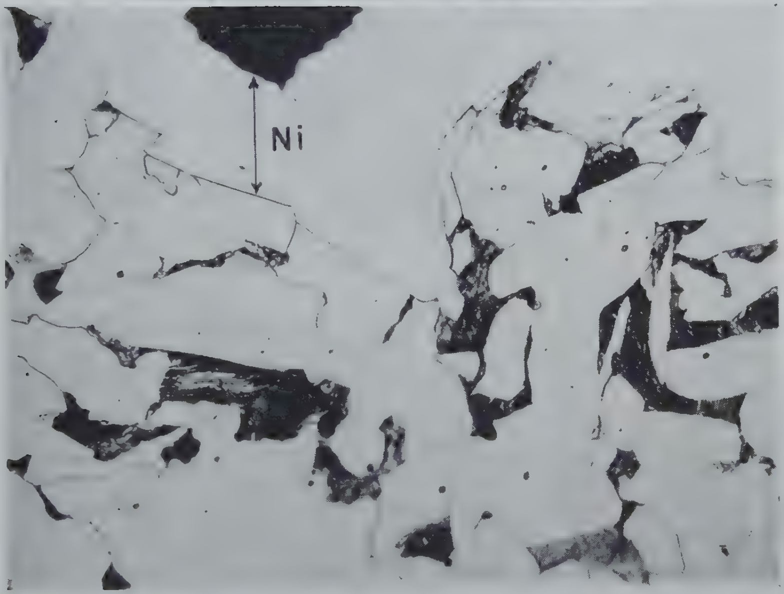


FIG 16—(above) The arrows indicate shock twins near the surface of a 90 pct "brittle" fracture.
Note that the shock twins and the cleavage facets occur at a slightly different angle. 1500 ×. Etchant 2 pct nital.

FIG 17—(below) Evidence that cleavage is sometimes arrested by pearlite colonies.
500 ×. Etchant 2 pct nital.

worthwhile to present it in an attempt to explain the differences between longitudinal and transverse energy values. It may be noted in Fig 1 that the energy curves for both longitudinal and transverse specimens start to rise at about the same testing temperature. Also, although the maximum energy values differ, both types of specimens reach their maximum energy value at about the same testing temperature. Furthermore, the macroscopic fracture appearance is similar for both longitudinal and transverse specimens at each testing temperature. These observations strongly suggest that the mechanism of the fracture is the same in both longitudinal and transverse specimens, but that the ease of fracture is altered by the well known anisotropy of rolled steel products such as the structural shape used in this work. We believe that the explanation of the ease of fracture in the transverse specimens is to be found in the ferrite banding in the steel.

In Fig 4, ferrite cleavage occurs quite generally throughout the "brittle" region of the fracture. This is the case for both longitudinal and transverse specimens of 80 pct and 90 pct "brittle" fractures. There is not much divergence of the energy curves in Fig 1 with these fractures.

The situation is quite different with fractures from the middle of the transition. In these fractures ferrite cleavage is more prevalent in the ferrite bands, whereas the bands containing more pearlite show greater deformation before fracture. It may be that pearlite even arrests the cleavage. There is some evidence for this, as illustrated by Fig 17, where the cleavage that ends in the pearlite colony has not advanced. Instead, the steel to the right of the cleavage has deformed considerably after the formation of the ferrite cleavage. Whether pearlite stops the cleavage may be open to some question, although it seems to be the case.

It has been shown already that ferrite cleavage constitutes the initial stage of the failure. Now, in the transverse specimens the uninterrupted bands of ferrite lie roughly parallel to the surface of final fracture, as illustrated by Fig 18. It seems reasonable to suppose that there would be more ferrite cleavage in these bands in the initial stages of fracture than in the rest of the structure. In this case the

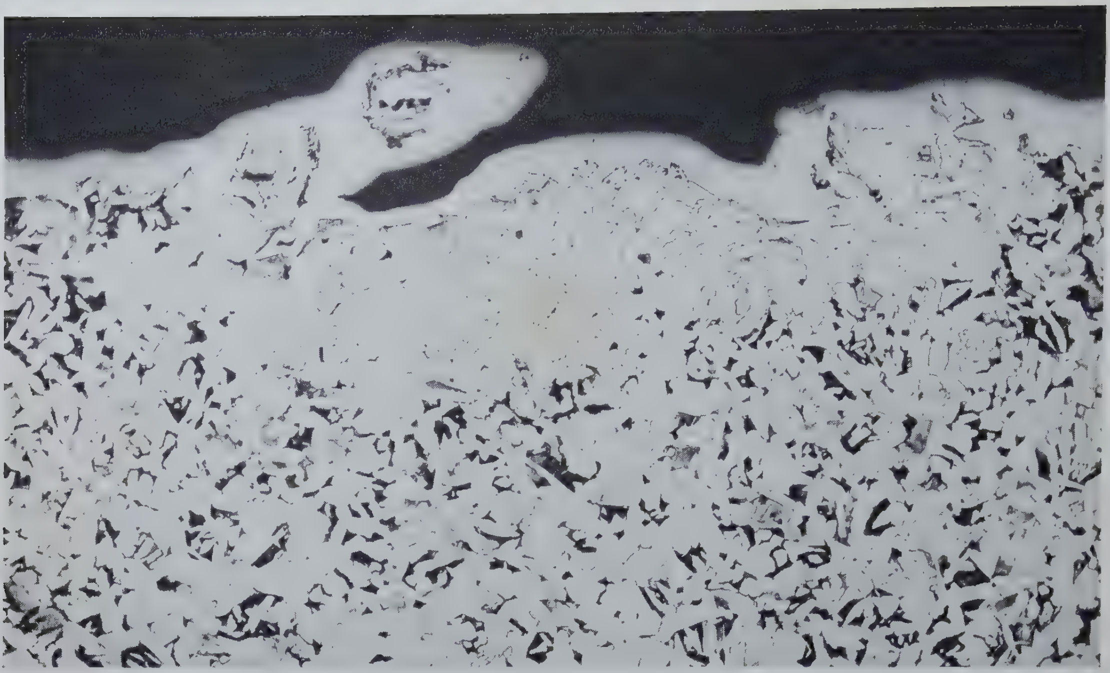


FIG 18—Cleavage in a ferrite band in a 50 pct "brittle" fracture of a transverse specimen.
100 ×. Etchant 2 pct nital.

ferrite bands would form a potential path of fracture, only needing to be joined by rupture of the intervening bands that contain pearlite. This explanation assumes a greater amount of ferrite cleavage in the "brittle" part of the fracture of transverse specimens, in order that the absorbed energy of the transverse specimens be less than for the corresponding longitudinal specimen in the middle and upper portions of the transition range. This was not checked quantitatively because of the experimental difficulties involved, so that the above explanation is to be considered only as a reasonable assumption based on the observed mode of fracture.

Summary

It cannot be too strongly emphasized that the fractures that have been described were observed in impact specimens from a single structural steel shape. The essential details of the mode of fracture are thought to be common to mild steel of this type, but more observations are needed to round out the general picture.

Throughout the transition revealed by the impact test, fracture in this steel was initiated by cleavage of ferrite grains situated in the general region of maximum triaxiality of stressing during the test. At the low temperature end of the transition, ferrite cleavage occurred during or soon after the end of elastic deformation. It was often accompanied or preceded by shock twinning of the ferrite. At higher testing temperatures within the transition, shock twinning gave way to deformation by slip. In the high temperature end of the transition, cold work apparently occurred both before and after the ferrite cleaved.

After the initiation of the fracture by ferrite cleavage, a second stage of the fracture consisted of opening up the ferrite cleavages and deformation and rupture of the metal between the cleavages. Deformation and rupture of the peripheral regions of the specimen also formed a part of the second stage of fracture.

The experimental observations suggest that hard phases such as cementite and inclusions are not to blame for initiating ferrite cleavage in mild steel. In fact, there was some evidence that pearlite could arrest ferrite cleavage and confine it to a ferrite band, at least in the middle and the high temperature end of the transition.

The tendency for the initial ferrite cleavage to extend quite generally throughout the ferrite band and the directional extent of these bands in rolled mild steel products is offered as a possible explanation of the difference in the energy values obtained with longitudinal and transverse specimens.

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Recovery and Recrystallization in Brass

B. L. AVERBACH,* Junior Member AIME

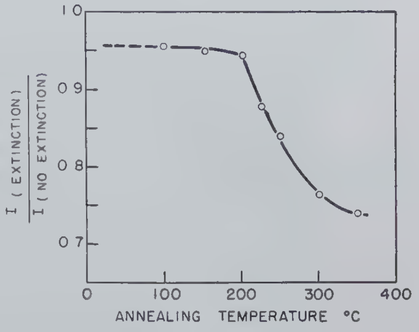
Recovery and primary recrystallization in cold worked metals are usually considered as two competing processes. Some of the effects which usually accompany recovery are: alleviation of stress corrosion tendencies, changes in thermal emf,[1] damping capacity,[2] electrical resistivity,[2] and magnetic properties,[3] and only minor changes in hardness or the related strength properties. During primary recrystallization new unstrained grains are formed at the expense of the strained matrix. These new grains eventually become visible metallographically, and nucleation and growth kinetics have been indicated for this process.[4,5]

Frequent attempts have been made to study the cold-working phenomenon by observations on the line broadening by X ray diffraction patterns. Relatively few measurements of line intensities have been made, although Brindley and his collaborators,[6,7,8] by means of film techniques, compared the intensities of cold worked Cu, Ni, and Rh patterns with those from chemically precipitated powders. These precipitated powders were presumed to be strain free, and it was found that the intensities for the cold-worked materials progressively decreased as the Bragg angle increased except for the first line, where there was an increase due to reduction in extinction. This was interpreted as a randomness in atomic position induced by cold work. Such randomness is similar to that caused by thermal agitation and has been described as "frozen heat" displacement of 0.08–0.10 Å from the mean atomic position.

In a recent study[9] on the effect of cold work in metals on their powder pattern intensities, the changes in integrated intensity for heavily cold worked alpha brass were observed as a function of the annealing temperature. These measurements were made with a manually operated Geiger-counter spectrometer using CuKα radiation monochromated with a rock salt crystal. Intensity measurements were made with a scaling meter over small intervals of angle, and the equipment was so arranged that the diffracted and incident beams made equal angles with the specimen. Intensities could be compared directly by simply interchanging specimens, and comparisons from day to day were made with a standard whose line intensities did not change on aging. It was shown that a cold worked alpha brass standard was stable for at least a year.

Table 1 indicates the results of the integrated intensity measurements on a 70 Cu-30 Zn brass. In the sample preparation, a brass plate was first cold rolled 50 pct and then filed, screened to −325 mesh, compacted into briquettes at a pressure of 60,000 psi and finally annealed for one hour at various temperatures up to 400°C. The briquetting pressure did not seem to influence the integrated intensities, and most of the cold work was introduced by the filing. Although this method of cold work is not quantitative, it was used to obtain random orientation (and thus uniform diffraction lines) in order to make accurate measurements of integrated intensity. Back reflection patterns were taken in each case to check the uniformity of the lines, and from the observed line broadening it was apparent that this type of plastic deformation was quite severe.

Care was taken to traverse the entire background of the pattern and to assign to each peak the total intensity above this background. The bases of the diffraction lines were quite broad and spread out over several degrees, even for the narrow peaks. The theoretical intensities were calculated to include a temperature correction, a dispersion correction, and a Lorenz-polarization factor corrected for the crystal monochromated beam. In Table 1 it was necessary to match the calculated and observed values at only one point, and the rest of the experimental values were converted directly to this arbitrary scale. The integrated intensities in Table 1 are listed in arbitrary units, and the accuracy was sufficient to reproduce any of the measured line intensities to within ±1.5 units. It is evident that the percentage error on the strongest line (111) was quite low.



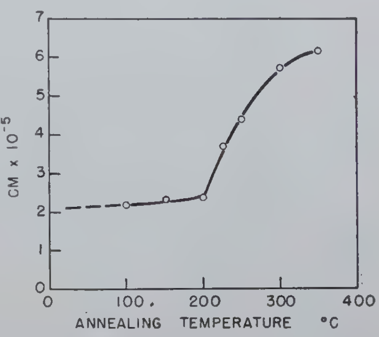


FIG 1—(above) Change of extinction coefficient with annealing temperature for cold worked brass (70 Cu-30 Zn).
FIG 2 (below)—Effective particle sizes calculated from extinction coefficients.

The calculated values and the observed intensities for the cold worked material matched reasonably well. As the annealing temperature was raised, however, the intensity of the strongest reflections, particularly the (111), decreased measurably. Since the background intensities of all of these patterns were identical, such behavior could be interpreted as a primary

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* Assistant Professor, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

[1] References are at the end of the paper.

Table 1 . . . Effect of Cold Work and Annealing on Integrated Intensities of X ray Diffraction Lines

Brass (70 Cu-30 Zn)—Cold Worked at 25°C

Line	Calculated Intensities	Annealing Temperature °C						
		25	100	200	225	250	300	350
(111)	193 ⇔	193	184	182	170	162	148	143
(200)	93.6	89.5	87	85	86	84	76	75
(220)	50.5	48	48	48	46	47	43.5	41
(311)	57.1	57.5	55	55	54	55	53	48
(222)	16.5	18.3	19.1	17.1	15.7	16.1	15.7	13.1
(400)	10.0	9.6	8.4	8.7	10.6	8.7	9.6	8.7

⇔ Indicates where calculated and measured intensities were matched.

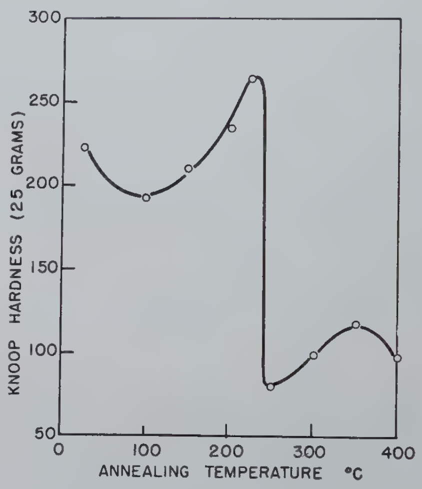

FIG 3—Tukon Hardness (25g load) of brass filings.

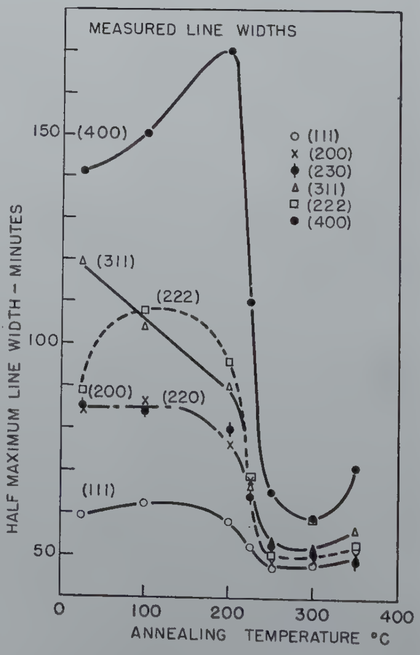

FIG 4—Change in half-maximum line widths with annealing temperature in brass (70 Cu-30Zn).

extinction effect, and it is apparent that cold work reduces this extinction considerably. The calculated values take no account of extinction, and the agreement between the cold worked and calculated intensities indicates that the deformation induced by filing was severe enough to practically eliminate extinction. The extinction coefficient, $\frac{\text{I (with extinction)}}{\text{I (without extinction)}}$, was calculated from the (111) lines, since the accuracy is greatest here, and these coefficients are plotted in Fig 1.* There is a sharp break at 200°C, and this sudden increase in extinction was subsequently associated with the onset of primary recrystallization.

The data presented in Table 1 are not sufficiently accurate to determine whether the intensities of the back reflection lines in the cold worked material were measurably lower than those of the annealed samples. The observations listed here were made in such a way as to accentuate the accuracy of the low angle high intensity lines. When more accurate intensity determinations were made in the high angle region,[9] it was shown that both cold worked and annealed materials diffracted the same integrated intensity for the relatively weak (400) line if all of the intensity above the true background was considered. The determinations based on film measurements can suffer inherent difficulties in the comparison of intensities from one film to another, and in the determination of the true background. These discrepancies may be sufficient to account for the diminished intensity originally observed in the high angle lines of cold worked materials.

In order to determine the cause for the sudden change in the extinction curve in Fig 1, observations were made on the hardness, the half-maximum diffraction line width, and on the metallographic structure. For the hardness test, the surfaces of the compacts were first given a metallographic polish with diamond dust and a large number of Tukon hardness readings were made on the individual filings at a load of 25 g. Although some scatter was obtained because of insufficient support under individual filings it was felt that the hardness readings from one specimen to another were comparable and the results are plotted in Fig 3. Each point in the figure is the average of at least five readings. The sharp dip in the hardness at about 225°C is usually taken as indicating the inception of primary recrystallization. Similarly the half-maximum line widths (plotted in minutes) also fall rapidly at about 225°C and this is indicated in Fig 4. It should also be noted that prior to this sharp dip the lines did not behave in uniform fashion, some lines increasing in width and others decreasing in width as the recovery temperature was raised.

From the microstructures, which are shown in Fig 5 and 6, it is difficult to determine the inception of recrystallization. Because of the heavy cold working the recrystallized grain size is very small and although there seems to be a subtle difference between the structures at 200 and 225°C, the strain-free grains are not observed in the microstructure until considerable growth has occurred. The X ray pattern first became spotty after a 400°C treatment and the microstructure in Fig 5 indicates that visible growth has occurred by then. The combined evidence can be taken, however, to indicate that recrystallization takes place starting at 225°C.

It is difficult to assign directly the cause for the reduction in primary extinction by plastic flow in a crystal. Above 200°C, recrystallization, and therefore grain growth, is involved and the extinction could be assumed to be a particle size effect. If the classical Darwin formula* is applied to these data one obtains an "effective particle size" of $2\text{-}6 \times 10^{-5}$ cm. These particle sizes are plotted in Fig 2 as a function of annealing temperature, and if the data are extrapolated below 100°C, one obtains an effective particle size of 2×10^{-5} cm at room temperature. Each of the measured particle sizes

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* The point at 150°C was determined from a measurement of the integrated intensity of the (111) line. The rest of the pattern was not measured and is, therefore, not listed in Table 1.

* $\frac{\text{I (with extinction)}}{\text{I (without extinction)}} = \frac{\tanh xq}{xq}$

x = no. of planes taking part in the reflection
q = reflected amplitude per lattice plane

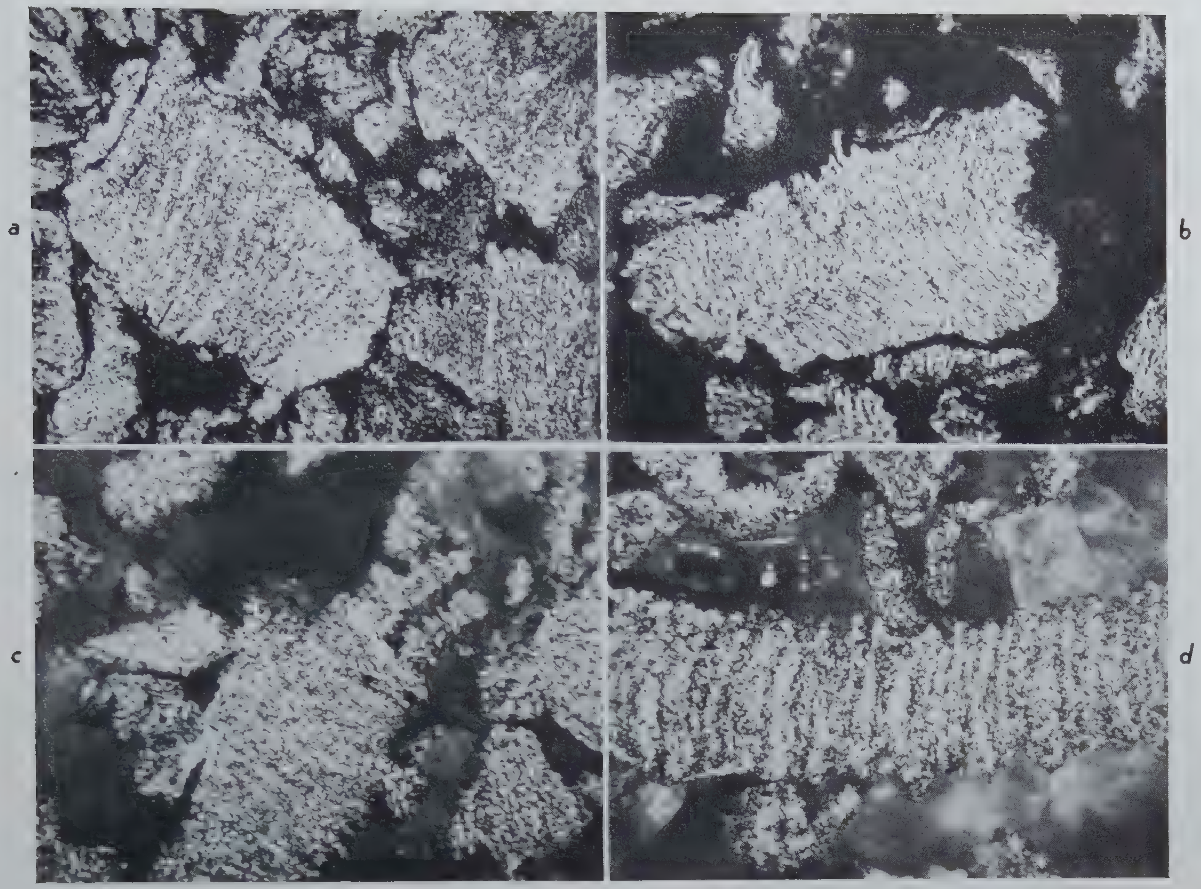

FIG 5—Micrographs of brass filings. 750 ×.

a. Cold worked. *b.* Annealed 1 hr at 150°C. *c.* Annealed 1 hr at 200°C. *d.* Annealed 1 hr at 225°C.

is accurate to at least one significant figure and if the experimental error in the measurement of the cold worked (111) line is computed it can be seen that the cold worked particle size is probably not smaller than 1×10^{-5} cm and is probably closer to the extrapolated value of 2×10^{-5} cm. If the recrystallized grain size is estimated at 400°C from the micrographs in Fig 6 one obtains about 20×10^{-5} cm. The X ray beam averages the extinction of both the cold worked and the annealed regions, so that for the entire specimen one obtains a weighted average value of about 7×10^{-5} cm and this fits the extrapolated X ray values quite well.

The presence of a nonuniform strain, even if it is an elastic strain, can also reduce extinction in crystals. It would be possible, therefore, to ascribe at least part of the extinction effect to nonuniform strains introduced by the deformation. However, Heidenreich and Shockley,[10] using an electron microscope technique obtained a particle size of about 0.2×10^{-5} cm in cold worked aluminum, and observed in addition a two stage process of growth. The first stage consisted of a rather slow growth of a few small strain-free areas, and this corresponded to the usual recovery stage. In the second stage a very rapid growth of strain-free areas occurred and this is the phenomenon usually observed during recrystallization. It would be difficult to interpret Heidenreich's results in terms of an overall strain relief, so that it seemed reasonable to assume that the small change in extinction during the recovery stage could have been caused by the slow growth of strain free areas by a method entirely analogous to what is later called recrystallization. Some overall relief would also occur simultaneously. Since recrystallization is a process of nucleation and growth the early stage corresponds to a prolonged incubation period and it seems unnecessary to specify a separate mechanism for recovery. The data presented here, however, are not accurate enough to show definitely whether there is a slow growth of particle size during recovery, and a more extended study on materials with a greater temperature range for recovery is needed.

Table 2 . . . Broadening of X ray Diffraction Lines in Brass (70 Cu-30 Zn) Cold worked at 23°C and annealed for 1 hour at temperatures indicated.

Line	θ°	Annealing Temperature °C				
		25	100	200	225	250
		Reduced Line Widths—(min.)				
(111)	21°10′	36	39	33	20	0
(200)	24°35′	68	70	58	30	0
(220)	36°10′	80	68	63	40	14
(311)	43°47′	101	90	74	44	15
(222)	46°20′	72	91	77	36	
(400)	56°30′	118	138	157	94	30

These data do indicate, however, that the most important process during the recovery stage may not be stress relief. If any substantial stress relief had occurred, it would have been reflected in a rather large change in extinction coefficient prior to recrystallization. Since the extinction remained virtually constant during recovery, it is suggested that the mechanism of recovery consists of the slow growth of existing strain free nuclei with a linear dimension of about 2×10^{-5} cm.

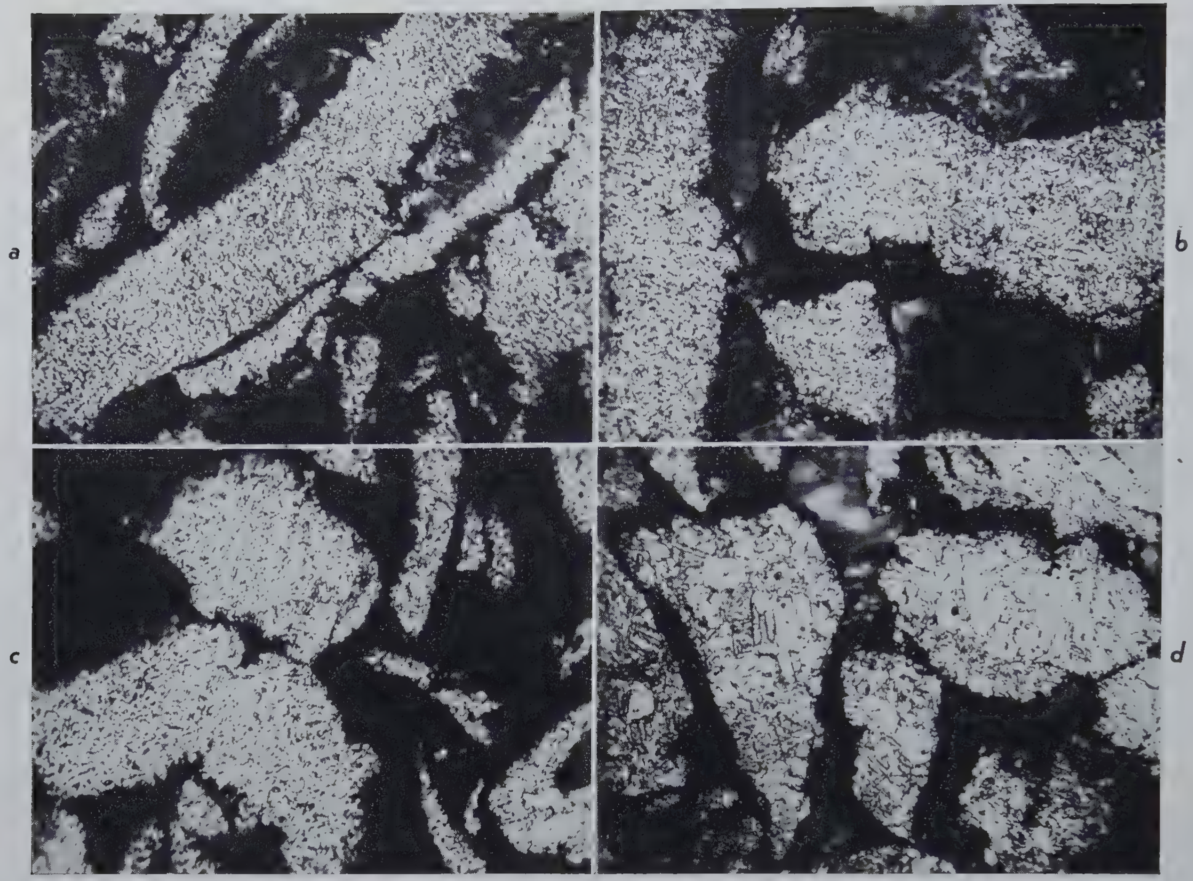

Fig 6—Micrographs of brass filings. 750 ×.

a. Annealed 1 hr at 250°C. *b*. Annealed 1 hr at 300°C. *c*. Annealed 1 hr at 350°C. *d*. Annealed 1 hr at 400°C.

The line broadening observed for these cold worked materials is also consistent with such an interpretation. Perfect crystals have a very narrow range of perfect reflection, but if the crystal is cold worked, the intensity distribution can be taken as an indication of the deviation from ideality of the radial distance to successive nearest neighbors. As recrystallization starts, certain small regions become strain-free, they reflect sharply, and the line broadening decreases.

The half-maximum line widths were reduced to include only the broadening due to cold work by assuming that the lines at 300°C and beyond did not contain cold work broadening. Then: B (due to cold work)

$$= \sqrt{B^2 \text{ (cold worked) } - B^2(300°\text{C})}$$

and the resulting line widths are shown in Table 2. It has been suggested that the cold-work broadening should be a linear function of tan θ, and Fig 7 indicates that there is too much scatter in the data to check this concept. Greater precision in line widths is needed to put this phase of the work on a more satisfactory basis.

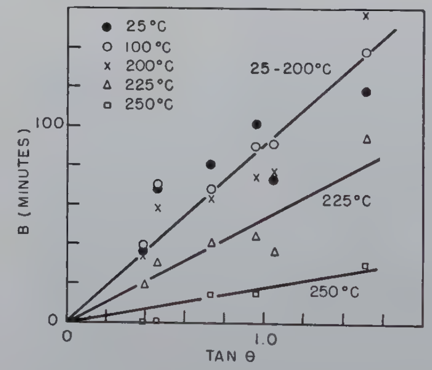

FIG 7—Line broadening due to cold work in brass (70 cu-30 Zn).

Annealed 1 hr at temperatures indicated.

Summary

On the basis of X ray extinction measurements it is concluded that recovery may be a process analogous to recrystallization. It is possible that small strain-free grains are formed during recovery, and that recrystallization is observed to occur when there is a rapid growth in the size of these strain-free regions. Recovery and recrystallization could then be two stages of the same process, and it would seem unnecessary to prescribe a separate mechanism, such as strain relief, for the recovery stage.

Acknowledgments

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Ferromagnetic Alloys in the Systems Cu-Mn-In and Cu-Mn-Ga*

F. A. HAMES,† Junior Member and **D. S. EPPELSHEIMER,**‡ Member, AIME

The ferromagnetic copper-manganese-aluminum and copper-manganese-tin alloys (Heusler alloys) owe their ferromagnetism to the beta phases (body-centered cubic structure) in their respective systems.[1,2,3] The ternary beta phase regions in these systems are extensions of the beta fields of the binary copper-aluminum and copper-tin systems into the ternary models of the copper-manganese-aluminum and copper-manganese-tin systems respectively.

X ray analysis has indicated the presence of long-range order in the more strongly magnetic alloys.[3,4,5] The ideal ordered structure is obtained in alloys of compositions Cu_2MnAl and Cu_2MnSn; the copper atoms occupy positions at cube centers while the aluminum (tin) and manganese atoms alternate at cube corners. This atomic arrangement is illustrated in Fig 1. The compositions Cu_2MnAl and Cu_2MnSn are also those that show maximum magnetic saturation moment.[3,4,6,7] Departures from these compositions result in a decrease in the degree of order attainable and a decrease in magnetic saturation moment.

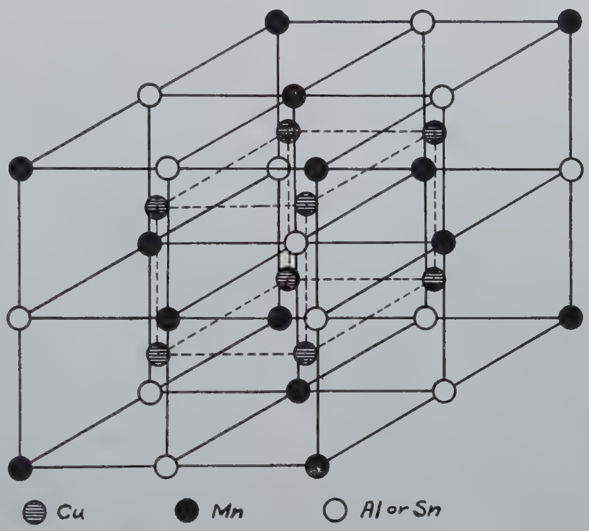

FIG 1—Atomic Arrangement in Ordered Beta Cu_2MnAl and Cu_2MnSn.

In view of the chemical similarities of aluminum, tin, indium, and gallium, and the existence of beta phases in the binary systems copper-indium and copper-gallium, it may be suspected that ternary beta phases exist in the systems copper-manganese-indium and copper-manganese-gallium, and that these are ferromagnetic. The purpose of this investigation was to determine whether ferromagnetic beta phases exist in the systems copper-manganese-indium and copper-manganese-gallium analogous to the ferromagnetic beta phases in the systems copper-manganese-aluminum and copper-manganese-tin.

Previous Work

At the time this investigation was started no information could be found regarding the constitution of copper-manganese-indium and copper-manganese-gallium alloys, nor of the binary manganese-indium and man-

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† Assistant Professor of Metallurgy, The University of British Columbia, Vancouver, B.C., Canada. Formerly Research Fellow in Metallurgy, Missouri School of Mines and Metallurgy, Rolla, Mo.

‡ Professor of Metallurgical Engineering, Missouri School of Mines and Metallurgy, Rolla, Mo.

[1] References are at the end of the paper.

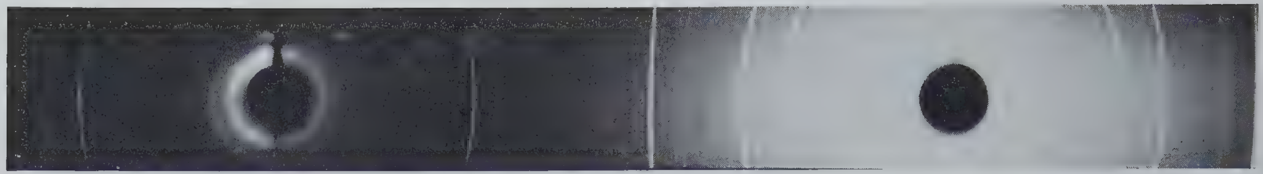


FIG 2—X ray Diffraction Pattern of Copper-Manganese-Indium Alloy I-1, Quenched from 500°C.

ganese-gallium alloys. The general features of the equilibrium diagrams of the systems copper-indium and copper-gallium are known however, and these are next considered with special reference to the beta phase fields.

SYSTEM COPPER-INDIUM

Weibke and Eggers have worked out a constitution diagram for the copper-indium system on the basis of thermal, microscopic, and X ray studies.[8] These investigators showed by X ray analysis that the beta phase in this system has the body-centered cubic structure. Powder diffraction photographs of quenched beta alloys taken at room temperature showed extra diffraction lines indicative of a superlattice.

Hume-Rothery and coworkers reinvestigated the beta phase area in the copper-indium system,[9] their beta phase field boundaries being in good agreement with those of Weibke and Eggers. High temperature X ray powder photographs taken by Hume-Rothery and coworkers of alloys in the homogeneous beta area showed only the lines to be expected from a simple body-centered cubic structure. They concluded that the extra lines on the films of Weibke and Eggers are characteristic of quenched alloys, rather than of the actual structure at high temperatures.

SYSTEM COPPER-GALLIUM

Weibke has published a constitution diagram for the copper-gallium system based on thermal, microscopic, and X ray studies.[10] Weibke reported a beta phase having a body-centered cubic structure, but that the beta copper-gallium alloys particularly resemble beta copper-aluminum alloys in that the structure of quenched alloys depends on the cooling velocity.

Hume-Rothery and Raynor[11] reexamined the constitution of copper-gallium alloys in the region 18–32 at. pct of gallium and published a diagram which shows a high temperature beta phase having boundaries that agree well with those of Weibke. Hume-Rothery and Raynor reported that the beta structure is retained by quenching from the homogeneous beta area only in alloys containing 22.5–23.8 at. pct of gallium. Beta alloys lying outside these composition limits decomposed on quenching. The same investigators also reported two modifications of the beta phase which they designated as beta′ and beta″, and suggested that a third modification exists below 420°C.

In later papers by Hume-Rothery and coworkers,[9,12] it appears that they have combined the beta′ and beta″ fields in a single field, representative of the beta phase (close-packed hexagonal structure). High temperature X ray powder photographs taken by these investigators showed that the beta phase has a simple body-centered cubic structure. They call attention to the fact that experiments with quenched alloys may give quite misleading results and point to the existence of a non-equilibrium phase having a simple close-packed hexagonal structure in alloys quenched from the homogeneous beta area.

Table 1 . . . Composition of Alloys Studied

Alloy Designation	Weight Pct			
	Cu	Mn	In	Ga
I-1	42.5	18.0	39.5	
G-1	49.5	21.6		28.9
G-2	62.3	13.0		24.7
G-3	57.8	16.0		26.2

Experimental

Alloys were prepared from copper of 99.99 pct purity; indium of 99.97 pct purity; Eagle-Picher gallium (purity not specified); and vacuum-sublimed or electrolytic manganese, both of 99.96 pct purity. The electrolytic manganese was treated for removal of hydrogen by heating at 500°C for one hour in a silica tube under a vacuum of 20 microns.[13]

One copper-manganese-indium alloy and three copper-manganese-gallium alloys were prepared and studied. The alloys were analyzed for copper and manganese and indium and gallium contents were obtained by difference. Analyses are listed in Table 1.

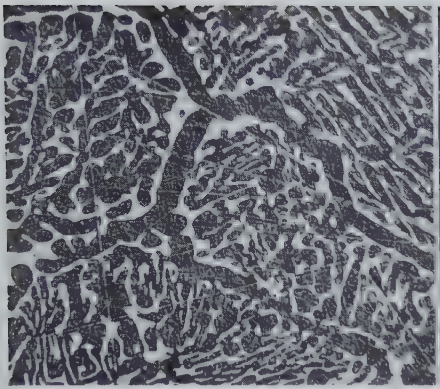
Alloy I-1 was prepared by melting indium and copper-manganese master alloy (composition Cu_2Mn) in an alundum thimble under a vacuum of 17 microns, with the use of a high-frequency induction coil. Alloy G-1 was prepared by melting copper, manganese, and gallium together in an alundum thimble under helium. Alloys G-2 and G-3 were prepared by remelting portions of alloy G-1 with added copper in evacuated Vitreosil tubes.

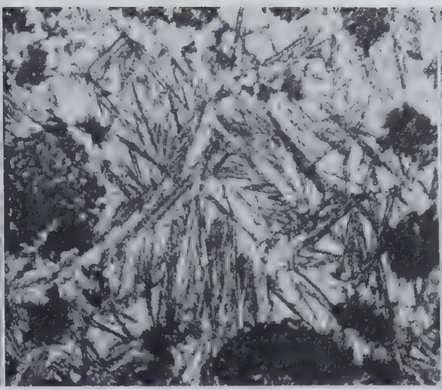
The compositions of alloys I-1 and G-1 were intended to correspond to atomic proportions Cu_2MnIn and Cu_2MnGa, respectively. Actual compositions as listed in Table 1 correspond to atomic proportions $Cu_{2.00}Mn_{0.952}In_{1.00}$ and $Cu_{1.97}Mn_{1.00}Ga_{1.05}$.

Alloy specimens for heat treatment were sealed in evacuated pyrex glass or Vitreosil tubes and heated in an electric pot furnace. Temperatures below 200°C were measured with a mercury thermometer, and temperatures above 200°C with a chromel-alumel thermocouple calibrated against the melting points of lead, zinc, and antimony. Temperature was adjusted by a Variac and was held within 10° of the desired temperature.

Powder diffraction photographs were taken with the Straumanis technique in a cylindrical camera of 57.3 mm diam. Unfiltered iron-K radiation from a Baird Associates X Ray Diffraction Unit was used. Powders were prepared from lump-annealed specimens and the powders were annealed as specified. The powder specimen was mounted in the camera on a glass fiber with the aid of vaseline, and rotated during exposure.

Approximate values of specific satu-





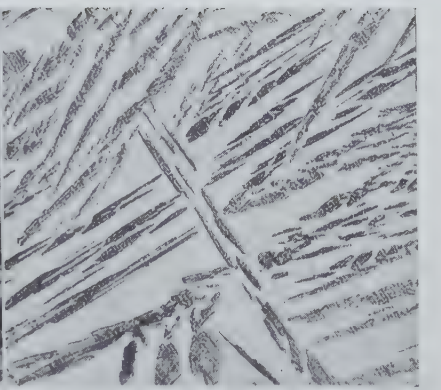


FIG 3—(left) Copper-Manganese-Gallium Alloy G-1, Quenched from 500°C. 100 ×
Potassium Dichromate Etch.

FIG 4—(center) Copper-Manganese-Gallium Alloy G-2, Quenched from 750°C. 100 ×
(Black Spots are Holes.) Alcoholic $FeCl_3$-HCl Etch.

FIG 5—(right) Copper-Manganese-Gallium Alloy G-3, Cooled in Furnace from 750°C. 100 ×
Potassium Dichromate Etch.

ration intensity of magnetization were measured at room temperatures with a magnetic balance constructed from an old magnetic ore separator. The balance is similar in design to balances used by Fereday,[14] Buehl and Wulff,[15] and Carapella.[16] The force per unit mass exerted on a small specimen placed in an inhomogeneous magnetic field is compared with the force per unit mass exerted on a standard specimen, in this case electrolytic nickel of 99.95 pct purity. The balance was arranged so that the force was exerted vertically and the force was measured with an analytical balance.*

Results and Discussion

SYSTEM COPPER-MANGANESE-INDIUM

The copper-manganese-indium alloy, I-1, was magnetic as prepared. Homogenized for three days at 500°C and quenched, this alloy was magnetic, and under the microscope appeared to consist of a single phase. The specimen was badly cracked and preparation of a suitable metallographic specimen was difficult.

Fig 2 shows the X ray diffraction pattern obtained from a powder specimen of alloy I-1 quenched from 500°C, and Table 2 summarizes the diffraction data for this alloy. Reflections were found which correspond to those expected for an ordered body-centered cubic structure with $a_0 = 6.206$ Å. This alloy appears to be structurally analogous to the ferromagnetic beta phases in the systems copper-manganese-aluminum and copper-manganese-tin. Following the analogy, an alloy of composition Cu_2MnIn, when fully ordered, would have an atomic arrange-

Table 2 . . . X ray Diffraction Data for Ferromagnetic Cu-Mn-In Alloy I-1

Radiation	hkl	$d_{obs.}$	d_{calc}	Intensity	
				Observed	Relative F^2pU
FeKα	†111	3.592	3.583	w	9.2
α	†200	3.108	3.103	ww	2.0
β	*220	2.196	2.194	ww	85.0
α	*220	2.190		s	
β	†311	1.868	1.871	ww	4.5
α	†311	1.868		w	
α	†222	1.790	1.792	ww	0.5
α	*400	1.548	1.552	m	26.0
α	†331	1.420	1.423	w	2.0
α	†420	1.395	1.388	ww	0.6
α	*422	1.266	1.267	m	33.0
α	†{511 333}	1.194	1.194	w	2.0
β	*440	1.096	1.097	ww	19.0
α	*440	1.098		m	
$α_1$	†531	1.049	1.049	w	4.2
$α_2$	†531	1.049		ww	
$α_1$	†{600 442}	1.034	1.034	w	1.5
$α_2$	†{600 442}	1.037	1.034	ww	
$α_1$	*620	0.9814	0.9813	ss	100.0
$α_2$	*620	0.9812		w	

* Fundamental (body-centered cubic) lines.
† Superstructure lines.

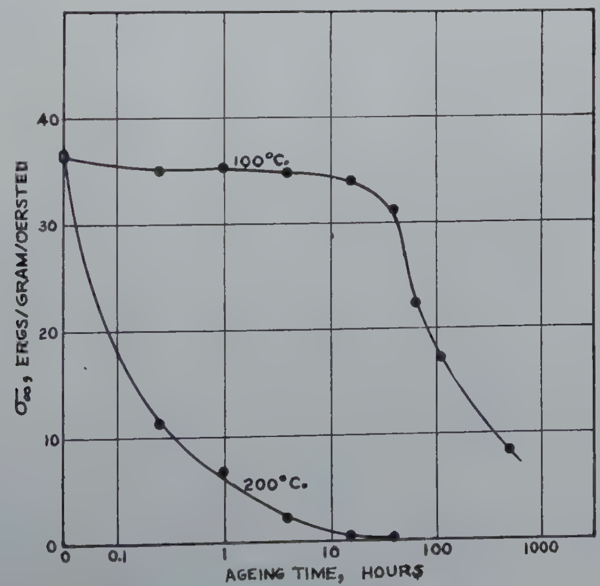


FIG 6—Effect of Aging on Saturation Magnetization of Copper-Manganese-Gallium Alloy G-3.

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* For details concerning the magnetic balance, see thesis.

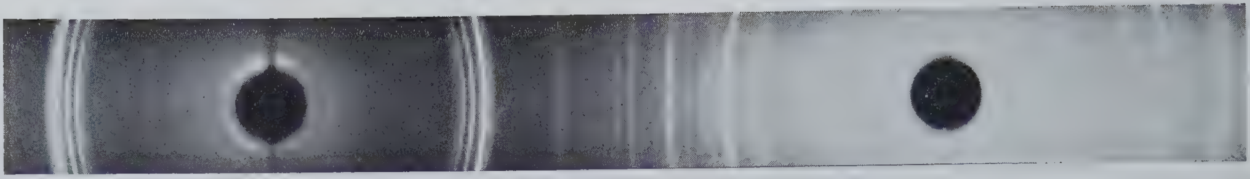

FIG 7—X ray Diffraction Pattern of Copper-Manganese-Gallium Alloy G-3, Quenched from 750°C.

ment like that shown in Fig 1 with indium atoms in place of aluminum (tin) atoms. This structure is based on space group O_h^5-Fm3m. Relative intensities were calculated as being proportional to F^2pU, where F is the structure factor, p is the multiplicity factor, and U is the Lorentz-polarization factor. These are listed in Table 2 together with visually estimated intensities for comparison. With the data at hand, nothing quantitative can be said about the degree of order in this alloy. It is certainly not fully ordered as it is deficient in manganese (composition $Cu_{2.00}Mn_{0.952}In_{1.00}$.)

After the present work was practically completed, the authors discovered an article by Valentiner and Pusicha[17] concerning the system aluminum-indium, in which mention was made of a ferromagnetic copper-manganese-indium alloy of composition Cu_2MnIn having the same structure as beta Cu_2MnAl and Cu_2MnSn. In a later brief paper,[18] Professor Valentiner has summarized his findings regarding the copper-manganese-indium system. He states that the composition Cu_2MnIn shows the highest intensity of magnetization. The structure is the same as that of Cu_2MnAl and Cu_2MnSn, with $a_0 = 6.2$ Å. This alloy has a very small hysteresis and coercive force (less than 0.4 oersted). The specific electrical resistivity is about three times as great as that of iron. The alloy is very brittle. The Curie temperature is about 270°C. Thermal treatment has but a very slight effect on the magnetic properties of copper-manganese-indium alloys, in contrast to the behavior of the copper-manganese-aluminum and copper-manganese-tin alloys.

SYSTEM COPPER-MANGANESE-GALLIUM

The copper-manganese-gallium alloy G-1 was not magnetic as prepared, and a series of heat treatments was therefore carried out to determine whether it could be rendered magnetic. Specimens were quenched from temperatures between 500°C and 750°C and aged at 100°C and 200°C for times ranging up to 110 hr following quenching. Saturation magnetization was measured after quenching and at intervals during aging.

Table 3 . . . X ray Diffraction Data for Alloy G-3, Quenched from 750°C

Intensity	Radiation	d
ww	FeKα	2.446
ww	β	2.294
m	α	2.286
ww	β	2.122
s	α	2.127
m	β	2.019
ss	α	2.018
m	α	1.968
m	α	1.556
m	α	1.532
m	α	1.371
ww	β	1.328
m	α	1.335
ww	β	1.292
s	α	1.295
s	α	1.207
w	α	1.148
m	α	1.135
ss	α	1.108
m	α	1.076
w	β	1.062
m	α	1.067
w	α	1.011

The specimens were only feebly magnetic, as quenched, and the effect of aging on magnetization was very slight. A notable exception was a specimen quenched from 650°C. This had a saturation magnetization about 2½ pct of that of nickel as quenched. Aging at 100°C for 110 hr doubled this value while aging at 200°C reduced this value ten-fold.

All quenched specimens showed two constituents under the microscope. Fig 3 shows a typical microstructure. In view of the feeble magnetism of alloy G-1 and the complexity of interpretation of the microstructure, this alloy was abandoned. The composition of alloy G-1 corresponds to atomic proportions $Cu_{1.97}Mn_{1.000}Ga_{1.05}$. It will be a matter of interest to determine whether an alloy of exact composition Cu_2MnGa ever exists as a single phase, analogous to the beta phases of compositions Cu_2MnAl, Cu_2MnSn, and Cu_2MnIn.

Alloys G-2 and G-3 were prepared by remelting portions of alloy G-1 with added copper. After homogenizing for 15 hr at 750°C the alloys were quenched in water and examined under the microscope. Both alloys showed an acicular (martensitic) structure and there was no evidence of the presence of more than one constituent. This is illustrated in Fig 4.

Both alloys G-2 and G-3 were magnetic after quenching. Experiments were carried out on alloy G-3 to determine the effect of certain heat treatments on magnetization. A portion of this alloy, when cooled in the furnace, became nonmagnetic and under the microscope had the appearance of Fig 5. A transformation is indicated. This behavior is similar to that of slowly cooled copper-manganese-aluminum and copper-manganese-tin ferromagnetic beta alloys.

Specimens of the quenched G-3 alloy were aged at 100°C and 200°C, and magnetization measured at intervals. The magnetization of the specimen aged at 200°C decreased with aging time, and after 40 hr was very feebly magnetic. The effect of aging at 100°C was also to cause a decrease in magnetization but at a slower rate. This behavior is shown graphically in Fig 6.

X ray diffraction photographs were taken of powder specimens of alloy G-2 and G-3, quenched from 750°C. Similar patterns were obtained for the two alloys. Fig 7 shows the pattern for alloy G-3 and Table 3 lists interplanar spacings and visually estimated line intensities for this pattern.

The diffraction patterns could not be interpreted satisfactorily. In particular, no combination of lines could be found which is reconcilable with lines to be expected from a body-centered cubic structure, simple or ordered. The occurrence of martensitic structures in quenched alloys (Fig 4) suggests strongly that the high temperature equilibrium structure is not retained by quenching. The acicular structure of quenched beta copper-gallium alloys has been noted by Hume-Rothery and Raynor,[11] and it is quite possible that this behavior persists in the ternary beta copper-manganese-gallium alloys. Also, Weibke[10] noted the resemblance of beta copper-gallium alloys to beta copper-aluminum alloys which are known to develop martensitic structures on quenching.[19]

It is therefore suggested that the quenched alloys G-2 and G-3 consist of a transition phase derived from the beta phase of the system copper-manganese-gallium, the beta phase being stable at high temperatures but not retained by quenching. This description is based on indirect evidence: by analogy with beta copper-gallium and copper-aluminum alloys. It should be possible to clarify the structure of the ferromagnetic copper-manganese-gallium alloys with the aid of high temperature X ray diffraction data.

Summary

A ferromagnetic copper-manganese-indium alloy has been prepared having an ordered body-centered cubic structure, and it is probably structurally analogous to the ferromagnetic beta copper-manganese-aluminum and copper-manganese-tin alloys (Heusler alloys).

Ferromagnetic copper-manganese-gallium alloys have been prepared. An alloy of composition $Cu_{1.97}Mn_{1.000}Ga_{1.05}$ variously heat treated is feebly magnetic and has a two-phase structure. It is questionable whether an alloy of the exact composition Cu_2MnGa ever exists as a single phase analogous to the beta phases of compositions Cu_2MnAl, Cu_2MnSn, and Cu_2MnIn.

With higher copper contents, quenched copper-manganese-gallium alloys are strongly magnetic. Quenched alloys show martensitic structures and are tentatively described as consisting of a transition phase derived from the beta phase of the system copper-manganese-gallium, the beta phase being stable at high temperature but not retained by quenching. Quenched alloys lose their magnetism on aging. Slowly cooled alloys also lose their magnetism, and this loss is correlated with a transformation which is observable under the microscope.

Acknowledgments

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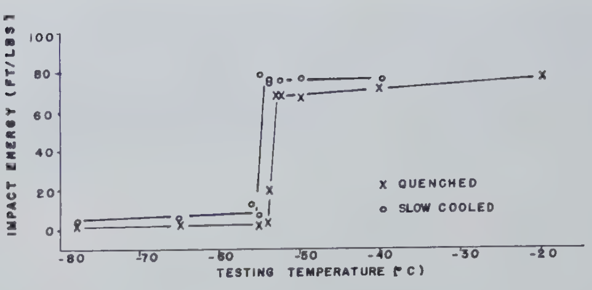
Effect of Carbon and Nitrogen on Temper Brittleness

D. C. BUFFUM,* L. D. JAFFE,* Junior Member AIME, and W. P. CLANCY*

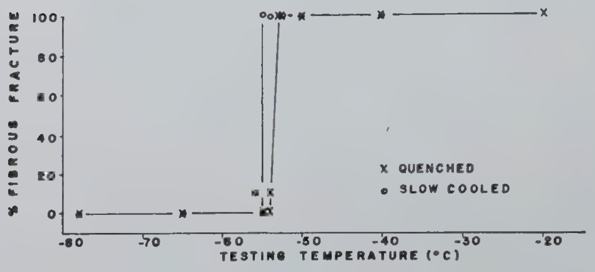
Many earlier workers have suggested that the temper brittleness of steel is associated with the presence of carbon or nitrogen.† Nevertheless, no investigations on the effect of removal of these elements upon susceptibility to temper brittleness have been published. It was therefore decided to determine whether temper brittleness would develop in an iron alloy containing very little carbon and nitrogen. The alloy,‡ in the form of a 10-lb ingot, was prepared by melting purified materials under argon. Its composition, in per cent, was:

C	Mn	Si	S	P	Ni	Cr	Mo	N	O	H
0.003	0.80	0.020	0.005	0.002	1.49	0.61	0.002	0.0004	0.017	0.00006

This analysis, except for carbon content, is within the specified range for SAE 3140, which has been demonstrated by previous work at this laboratory[2] to be markedly susceptible to



A. IMPACT ENERGY



B. PERCENT FIBROUS FRACTURE

FIG 1—Toughness vs. testing temperature curves for alloy of S.A.E. 3100 composition with 0.003 pct carbon.

temper brittleness.

Charpy blanks machined from the alloy were heat treated as follows:

°F °C
10 min. at 2100 (1150), water quench
10 min. at 1650 (900), water quench
30 min. at 675 (360), air cool
60 min. at 1250 (675)

Half the blanks were water-quenched from the final temper and half were furnace-cooled. The treatment produced an austenitic grain size of ASTM 3–2 and a microstructure which was entirely ferritic.

The blanks were machined to subsized V-notched Charpy specimens 7.5 mm square, 55 mm long, with a 45° V-notch 1 mm deep and having a ⅛ mm radius at its base.* The specimens were tested on a standard (217 ft-lb) impact machine, with the results given in Fig 1.

The transition temperatures of the quenched and slow cooled specimens were −53 and −54°C, respectively, as shown in Fig 1. Since these temperatures are the same within the limits of experimental error, the results are consistent with the view that temper brittleness cannot develop in the absence of carbon and nitrogen. It may be pointed out, however, that two alternative explanations are possible. First, embrittlement may occur so slowly that furnace cooling provides insufficient time for appreciable embrittlement. Second, embrittlement may occur so rapidly that complete embrittlement develops even on the water-quench from the temper.[2] In an alloy of the composition used, it is considered unlikely that either of these alternative views is valid.

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This note has been published by permission of National Military Establishment.
* Watertown Arsenal Laboratory, Watertown, Mass.
The statements or opinions in this note are those of the authors and do not necessarily represent the views of the Ordnance Department.
† These suggestions have been reviewed by Jolivet and Chouteau.[1]
‡ Made by National Research Corporation.
[1] References are at the end of the note.

It is interesting to note that the material used apparently does not quench-age, but the amounts of carbon and nitrogen present are sufficient to cause strain-aging.

Further work is planned on the same composition, as well as on alloys with carbon and nitrogen added separately and together, since an alloy to which carbon and nitrogen are added will still differ from commercial steel in phosphorus content.

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* Behavior of these specimens is compared with that of full-size Charpy bars in a forthcoming paper.[3]

Secondary Recrystallization in Copper

M. L. KRONBERG* and F. H. WILSON,† Member AIME

The low temperature recrystallization of very heavily rolled copper produces a fine grained structure with a high degree of preferred orientation. Additional heating to within a few hundred degrees of the melting point may induce an abrupt and pronounced increase in the grain size, with the resulting crystals having new orientations. This behavior at high temperatures is commonly termed "secondary recrystallization."

Several investigations have dealt with the phenomenon and have served to bare many features of the behavior.[1–4] In general, observations have been made on the sizes and shapes of the grains, and data have been presented showing the existence of an induction period in isothermal experiments.

Although it has been well established that the orientation before the change is statistically (100) [001], the so-called "cubically aligned" texture, there is no such agreement on the orientation after the change. For example, Dahl and Pawlek[1] describe it as being equivalent to an approximately 30° rotation about the [100] axis of the ideal cubic texture which is parallel to the rolling direction, the resulting orientation being near (210)[001]; and Cook and Richards[2] find an orientation of approximately (110)[112].

Since the completion of most of the work to be reported in this paper, Bowles and Boas[3] have published their very illuminating paper on "secondary recrystallization," in which they present convincing evidence for a third orientation and show that their experiments give no evidence for either of the other two orientations. The orientation is described as equivalent to an approximately 30° rotation about a [111] pole of the ideal cubic orientation.

The existence of a variety of reported orientations is not unique for copper, for a similar state of affairs exists for other systems that have been studied—aluminum, nickel, nickel-iron alloys, and others. It seems therefore that the existence of this variety does not necessarily constitute a contradiction, but rather indicates that different experimental conditions yield different results.

The fundamental nature of the phenomenon has not been elucidated. However, it has been generally recognized that the large grains could be the end product of growth of a few select grains already existing in the sample in minor amounts—too small to allow detection—or that entirely new ones could be formed by a process of nucleation and growth. Existing experimental evidence does not distinguish between these two most apparent possibilities. Nevertheless, the former has been more generally favored largely because our current understanding of the state of an annealed metal has not made it seem reasonable to expect a nucleation event to occur at temperatures above those required for the primary recrystallization.

Observations on the Preparation and Heating of Twin-bearing Cubically Aligned Copper

The starting material used throughout the investigation was a bar of OFHC copper, forged and annealed at 950°C. Visual inspection showed the grain size to be around 0.5 mm, and did not disclose any preferred orientation. A chemical analysis showed the following composition:

Cu + Ag— 99.99 pct
S — 0.005 pct
O — <0.005 pct

For the preparation of cubically aligned copper, ¾ in. thick slabs were cut from the bar, heavily pickled in concentrated HNO_3 and cold rolled to sheets about 0.012 in. thick. The reduction in thickness was approximately 98.5 pct. Standardized annealing techniques were followed. Samples to be heated were lightly dusted with alumina in order to prevent sticking and then sandwiched between $\frac{1}{16}$ in. copper plates. The resulting sandwich was heavily wrapped with copper sheet, and then annealed in air. The protection was such that only very thin films of oxide were formed. That the associated light oxidation of the samples had no specific effect on the recrystallization behavior was shown by the similar results that could be obtained on annealing in highly purified and dried hydrogen.

Two methods were used in bringing samples to temperature: (1) by placing the package directly in the furnace at temperature and (2) by placing the package in the furnace at room temperature, and then slowly increasing the temperature. The corresponding heating rates are illustrated in Fig 1, and will be referred to as "rapid" and "slow," respectively. Unless specified otherwise, all anneals will be of the former type.

Metallographic examination was made on samples prepared by electrolytic polishing and etching as described in the Metals Handbook.*

STRUCTURES FOUND BEFORE "SECONDARY RECRYSTALLIZATION" OCCURS

Annealing the rolled material for 1 hr at 400°C produced a heavily twinned, cubically aligned structure, the grain size being of the order of 0.03

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* Formerly Copper Research Lab. The American Brass Co; now Hammond Lab., Yale University.

† Copper Research Laboratory, The American Brass Co., Waterbury, Conn.

[1] References are at the end of the paper.

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* A.S.M. Metals Handbook, p. 901.

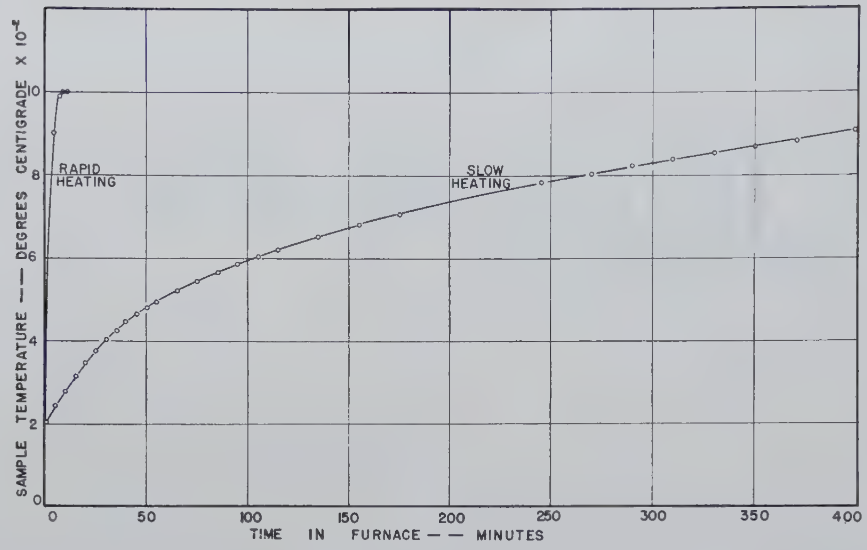

FIG 1—Rates of heating in two annealing techniques used for secondary recrystallization of copper.

mm. The effect of annealing at progressively higher temperatures was to cause an increasing consumption of the twins, and a moderate increase in the size of the grains. With a 1 hr anneal at 850°C the grain size increased to around 0.08 mm. Fig 2 illustrates the microstructure of the resulting material. Only a light etch is needed to reveal the twins, whereas the individual cubic grains as seen in the figure are revealed by a heavier etch. Still heavier etching develops the familiar aligned cubic etch pits characteristic of the material. The effect is illustrated in Fig 3.

Fig 2 also discloses that the grain boundaries are generally curved, and that there is a wide variation in the angles between the boundaries. These conditions indicate that the equilibrium state of grain growth by boundary migration has not been achieved.

The resolution of the grain boundaries between a grain and its various neighbors varies considerably, some of the boundaries being scarcely visible at all. This observation leads to the conclusion that there is a variation in the extent of mismatch in the relative positioning of the individual crystals—presumably the closer the match, the finer the grain boundary. Apparently the material can be described equally well as a very imperfect single crystal or as a polycrystal having a high degree of preferred orientation.

It has been observed that heavy rolling reductions cause the edges of the strip to tear and thus to form protruding "ears." When the rolling is completed these "ears" have undergone a different kind of deformation from the bulk of the material, and thus on recrystallization do not have a well developed "cubic" texture. On the other hand, the grain size within such a region after a 400°C anneal is approximately the same as that of the "cubic" grains. Annealing at higher temperatures, however, develops larger grains within the "ears," and indeed at temperatures of around 800–900°C the size is several fold larger. (Fig 4). Thus it can be concluded that grain growth in cubically aligned copper is very sluggish because of the great similarity in the orientations of the individual grains.

STRUCTURES RESULTING FROM "SECONDARY RECRYSTALLIZATION"

Although a 1 hr anneal at 850°C resulted only in grain growth of the cubic grains, heating samples for longer times, of the order of 2 hr, at 850°C sometimes induced "secondary recrystallization," thereby verifying the existence of an induction period. In general, in those samples showing the large grains, the treatment had not resulted in a complete absorption of the cubic material. Longer annealing

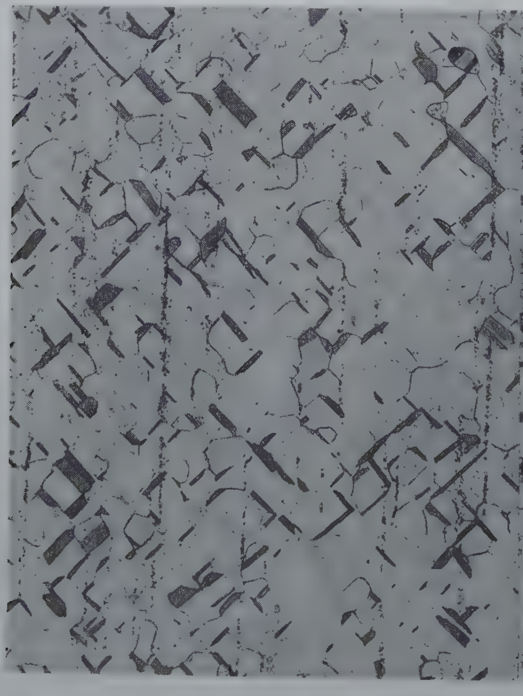

FIG 2 (left)—Structure of twin-bearing cubically aligned OFHC copper. Starting grain size approx. 0.5 mm, rolled 98.5 pct, annealed 1 hr at 850°C. 75 ×
FIG 3 (right)—Cubic etch pits in cubically aligned copper. 250 ×

times, of the order of 4 hr, were needed in order to complete the absorption, but growth always stopped at the "ears." The foreign orientations existing in these edge fragments could not be absorbed even by annealing for 4 hr at 900°C. Higher temperatures were needed for invasion of these areas and in general many of the grains resisted consumption even after annealing for 4 hr at 1000°C. Thus it is seen that the cubically aligned grains are absorbed much more readily than grains of other orientations.

Examination of numerous samples showing partial consumption of the cubic material revealed no specific tendency for growth to initiate at the "ears." Rather, growth almost always started within the body of the sample and then spread toward the edges. Thus there is a pronounced tendency for growth to start within the cubically aligned grains, rather than among the foreign orientations existing at the edges. Fig 4 shows two illustrations of the transition region between residual cubically aligned grains and those existing at an edge of a sample almost entirely converted to large crystals.

The shape of the boundary between a growing large grain and the residual cubic ones has been observed. It is illustrated in Fig 5. One sees that the boundary is scalloped, being pointed toward the boundaries of the cubic grains. Thus growth is proceeding in accord with the principles of boundary migration.[5,6]

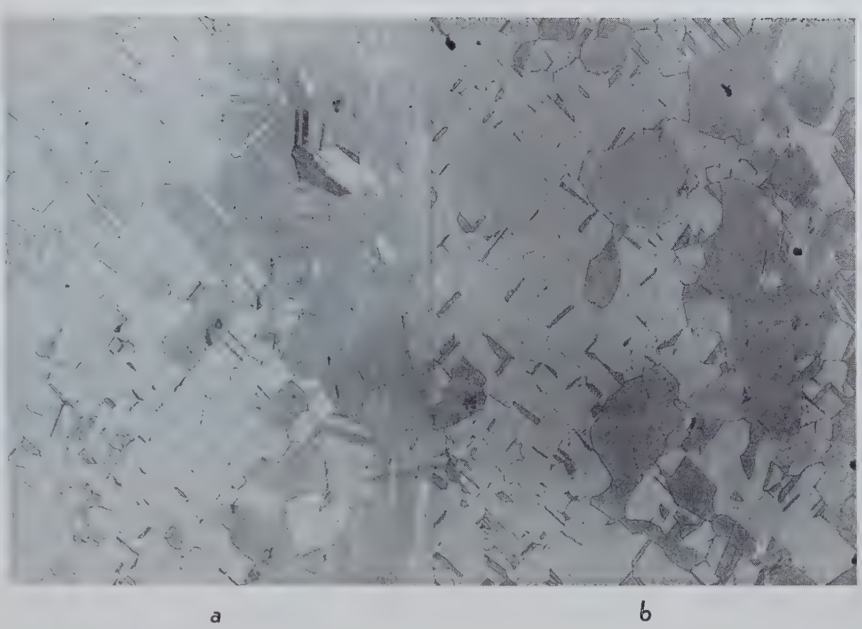

FIG 4—Structure of the transition region between cubically aligned copper and the more random orientations near torn edges.
75 ×. Reduced approximately one-third in reproduction.

Experimentation showed that for ultimate temperatures of 900–1000°C the sizes of the large grains are strongly influenced by the heating rate, the more rapid the heating the smaller the grain size. For example, slow heating often produced grains with from 1–8 sq in. in surface area, whereas the rapid heating produced grains with approximately $\frac{1}{16}$–$\frac{1}{4}$ sq in. Fig 6 illustrates typical samples formed by the two heating methods.

The illustrations show that the individual grains formed during "secondary recrystallization" have a highly preferred orientation. Two types are formed: those characterized by, (*a*) prominent twin traces at approximately 45° to the rolling direction, and (*b*) elongation parallel to the rolling direction and frequently showing no twins at all. The former are formed almost exclusively if the heating rate is rapid through the region of 800–1000°C and the latter form in minor concentrations if the rate is slow in this temperature region, or if rapidly heated samples are held at temperature in the

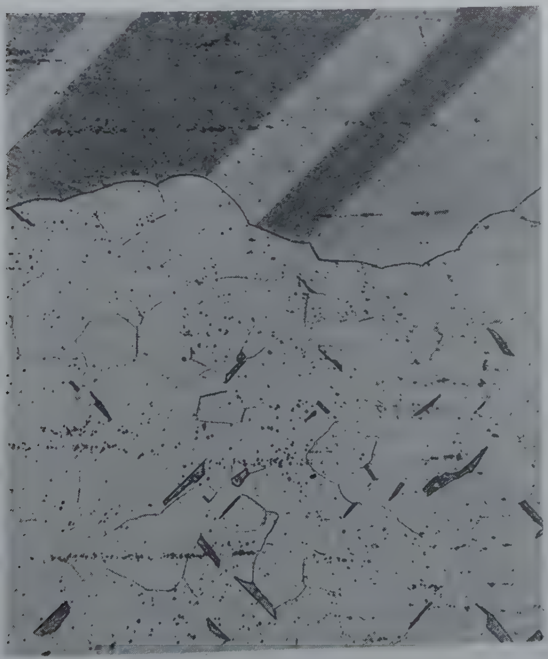

FIG 5—Advancing boundary of a large grain.
150 ×.

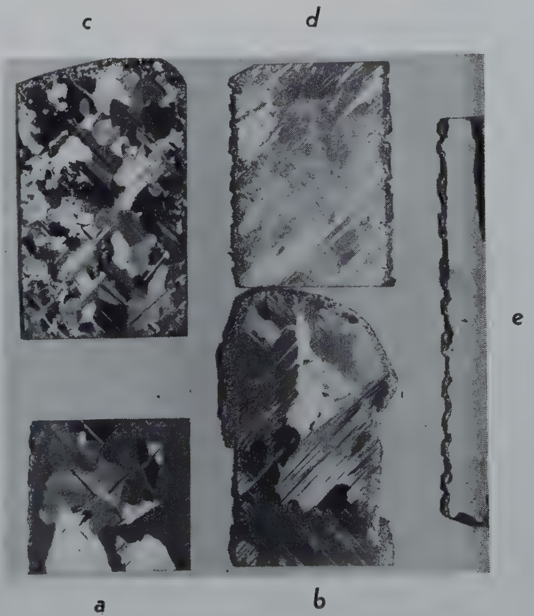

FIG 6—"Secondary recrystallization" of twin-bearing cubically aligned copper.
a. Rapidly heated to 900°C + 1 hr. *b*. Slowly heated to 900°C. *c*. Rapidly heated to 1000°C + 1 hr. *d*. Slowly heated to 1000°C. *e*. Rapidly heated to 1000°C + 1 hr. *b*, *d*, and *e* are particularly illustrative of stoppage of growth at torn edges. ⅔ ×.

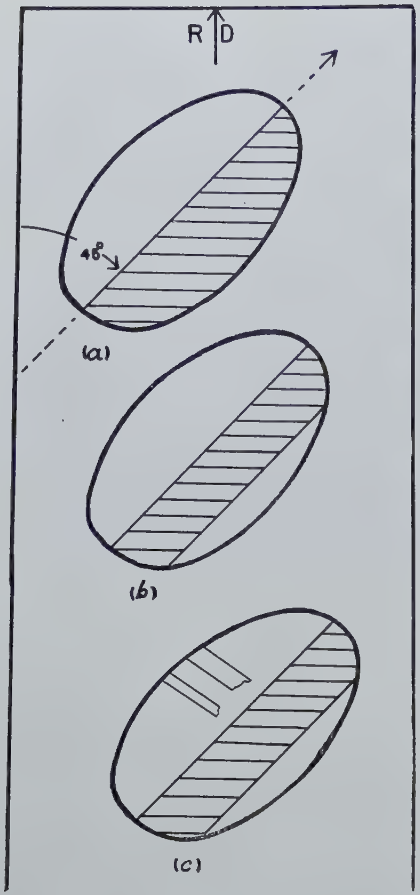

FIG 7—Schematic representation of grain shapes commonly found in rapidly heated samples.

region of 850–900°C. Examples of the latter type are the "white" grains at the upper and lower left of sample (*a*) and near the upper center of sample (*b*) in the figure.

A careful examination of the grains formed by rapid heating to 1000°C shows a tendency for the development of a characteristic shape and a characteristic positioning of the twin boundaries. It is convenient to describe the grains in terms of these fundamental characteristics, and Fig 7 illustrates the idealized shapes in a highly schematic way. The simplest shape (*a*) is an ellipse with the major axis coinciding with the trace of a twin boundary. Indeed, around 70 real crystals approximating such a shape and composed of a single twin pair have been observed. In a more common variety (*b*) one of the twins appears as a band dividing the grain about equally. Careful examination of grains with relatively thick bands has shown, however, that it is not the band which divides the grain, but rather one of its boundaries. Some of the grains (*c*) show additional twins within either or both of the components. Fig 8 (*a* and *b*) shows some particularly illustrative grains.

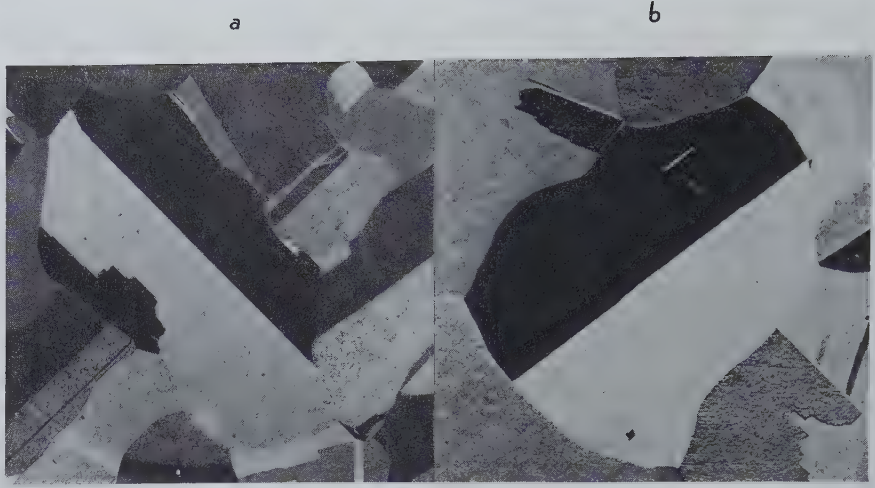

FIG 8—Elongated twinned grains found in samples rapidly heated to 1000°C.
Rolling direction vertical. 10 ×. Slightly reduced in reproduction.

The repeated appearance of roughly elliptical grains containing a twin boundary near the center and along the major axis suggests that growth develops a twinned crystal as the first unit of growth and continues most rapidly parallel to the twin boundary. If it occurs by the development of a grain already existing in the material, then this starting grain would be a single twin pair. If it occurs by nucleation and growth, then the nucleation would presumably occur at a twin boundary. During the growth, either member of the twin pair could twin on a parallel plane generating another unit of the complementary orientation, and both orientations could give rise to second generation twins on other (111) planes.

There are some observations indicating that growth initiates most readily at the surfaces of the samples and proceeds most rapidly parallel to the surface. Specimens displaying the early stages of growth show some grains extending over ¼ in. along the surface, but only a few thousandths of an inch below the surface. Others show grains extending ½ in. along the surface, but meeting other grains growing from the other surface approximately half way.

In brief summary, "secondary recrystallization" occurs after an induction period at temperatures above about 850°C in twin-bearing cubically aligned OFHC copper, the induction period being shorter at higher temperatures. Slow heating through the temperature range of 800–1000°C produces much larger crystals than rapid heating. The latter process produces one kind of orientation, type (*a*), and the former produces an additional one, type (*b*), in minor concentrations. Type (*a*) always contains a twin boundary at about 45° to the rolling direction, whereas type (*b*) frequently is twin free. When formed by rapid heating, the type (*a*) grain is often approximately equally divided by a twin boundary and is elongated in the direction of the boundary.

Growth of the large grains occurs readily in cubically aligned copper but is slowed drastically when grains of other orientation are met at the torn edges. There is no particular tendency for growth to initiate at the torn edges. The contour of the boundary of a growing grain is in accord with the predictions of the principles of grain growth by boundary migration.

CRYSTALLOGRAPHIC ORIENTATIONS RESULTING FROM "SECONDARY RECRYSTALLIZATION"

Orientations of the grains resulting from "secondary recrystallization" were determined using the back-reflection Laue technique of Greninger.[7] Eleven samples were used. Four were formed by "rapid" anneals for 1 hr at 900°C and seven by "slow" anneals at 950°C. The resulting orientations of both types of grains, (*a*) and (*b*), apparently were not affected by the variation in heating rate.

The analysis of the data showed that the position of the octahedral pole common to a twin pair (type (*a*) grain) is close to the position of one of the octahedral poles of the ideal "cubic" orientation. The location of this pole for 52 grains is plotted in stereographic projection in Fig 9, in which the plane of projection is the plane of the copper strip. The distribution of poles is shown in relation to the 5° radius circles around the [111] poles of the ideal "cubic" orientation. The plot is to be compared with Fig 10, showing a pole figure of the "cubic" texture plotted from X ray photograms of unconsumed material in one of the samples annealed at 900°C. For comparison, 5° circles are drawn around the [111] poles of the ideal orientation. The great similarity in the two distributions suggests that the orientations of the new grains may be formally related to those of the old by rotations around a [111] pole.

The character of the indicated rotations can be investigated rather simply if one confines the analysis to those poles falling within a densely populated region. For this purpose, the area defined by the 5° circles about the ideal cubic position has been selected. The positions of the corresponding central [100] poles of the selected crystals are plotted in Fig 11 after bringing their [111] poles into the same quadrant, and 5° circles are drawn to cover the most densely populated regions. By plotting the poles of both twins in some cases, a total of 63 orientations on 40 [111] poles is included. It is seen that nearly all the poles are enclosed by the circles, but that there is a spread of a few degrees in the directions of greater and lesser rotation. The corresponding distribution is roughly of the form that would be required for a discrete, or unitary, rotation, that is, one involving an exact angular relationship between each grain and its parent. The poles within the circle would arise from cubic grains whose [111] poles lie within the defined 5° circle, and whose central [100] poles would lie within a 5° circle about the ideal position of those poles. In the pole figure of cubically aligned copper, there is an appreciable concentration extending several degrees outside the 5° circle, and thus with unitary rotation the observed kind of spread would develop. An amount of rotation can be estimated by the angular distance from the center of the plot to the centers of the 5° circles. It is seen that the rotations are opposing ones of approximately 22 and 38°, the individual rotations corresponding to the members of a twin pair.

With one exception, specific directions of rotation are observed. Around the south-east and north-west [111] poles the 22 and 38° rotations are found to be clockwise and counterclockwise respectively, and for the other two poles the directions are re-

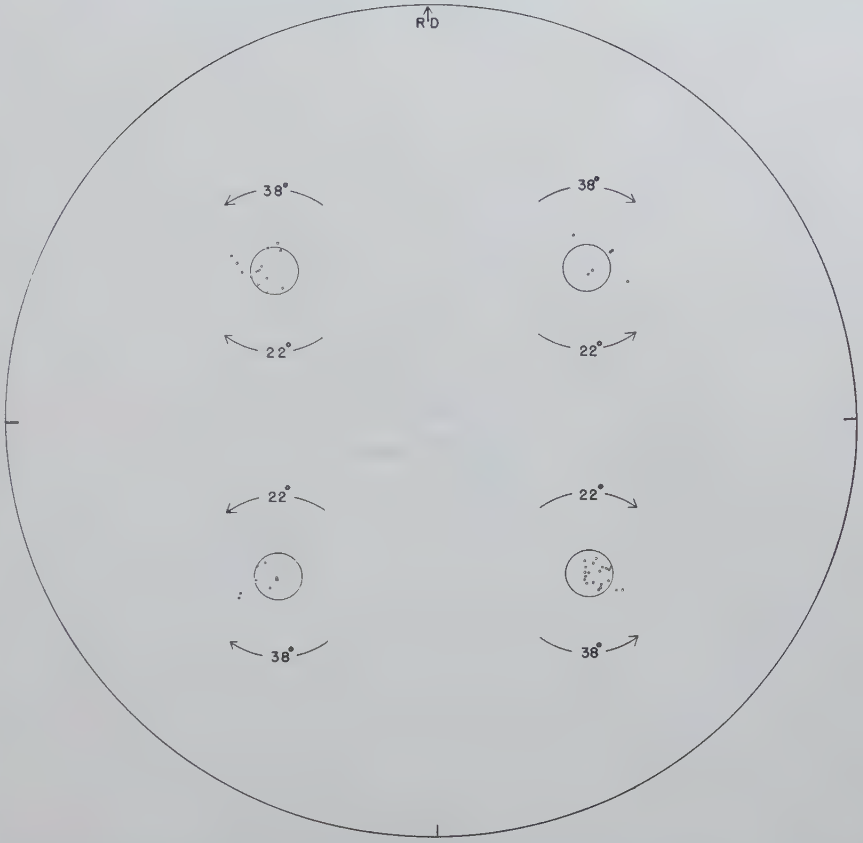

FIG 9—The positions of the [111] poles of 52 large crystals which lie near the [111] poles of (100)[001].

± 5° circles are centered on the [111] positions of (100)[001].

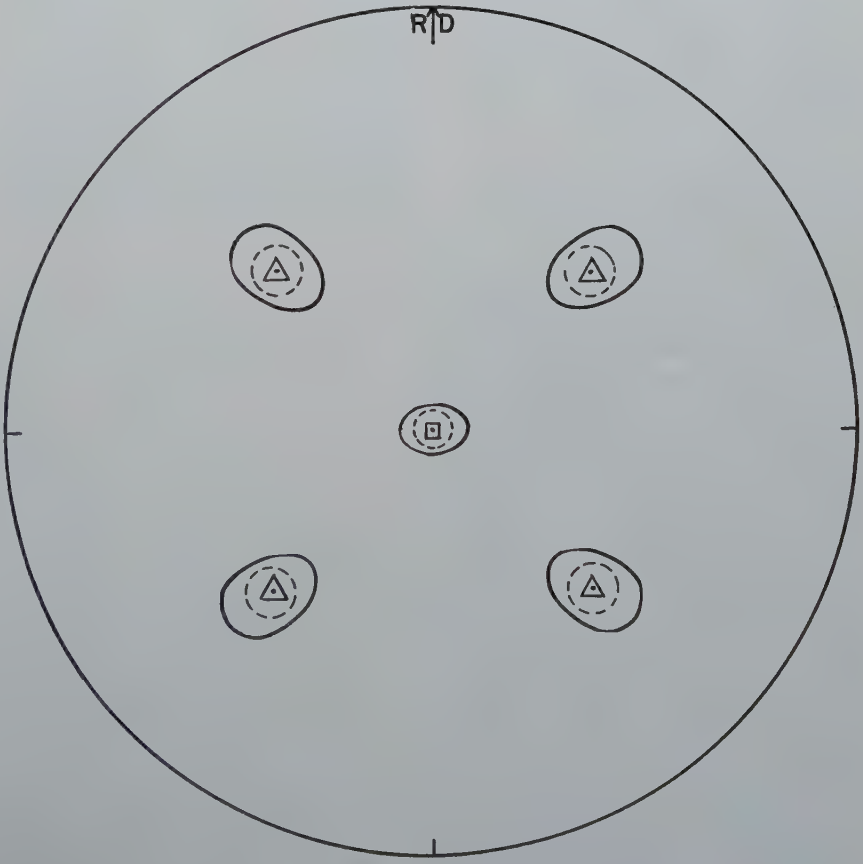

FIG 10—Pole figure of cubically aligned copper.

Broken ± 5° circles give indication of extent of deviation from (100)[001].

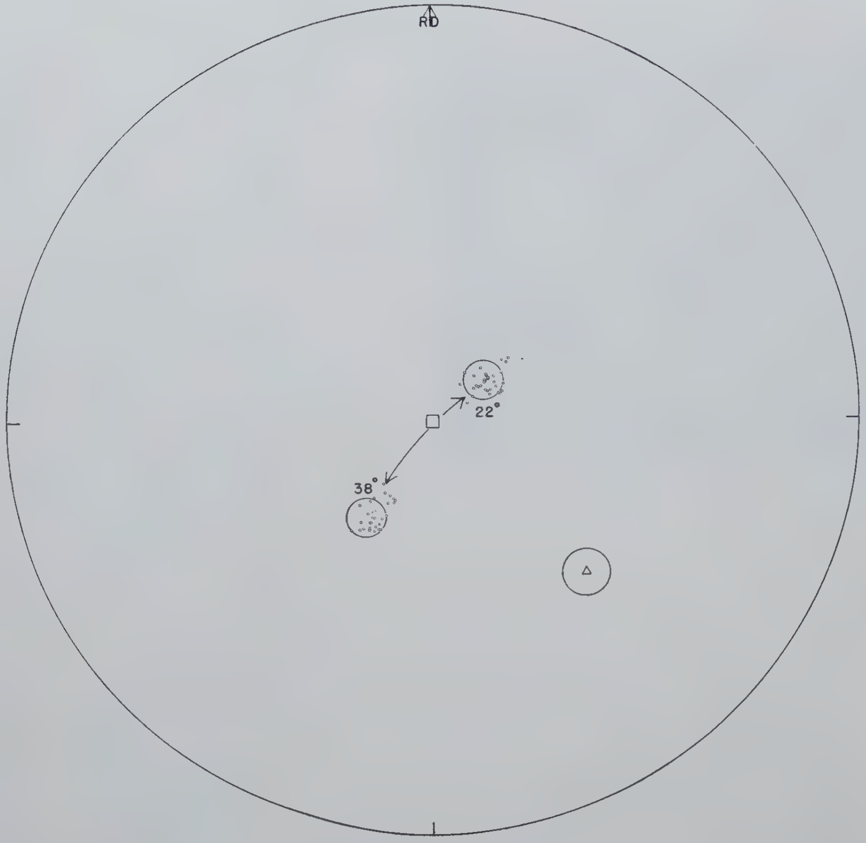

FIG 11—The positions of the central cube poles of 63 large crystals which are derived by rotation about [111].

Centers of ± 5° circles are at indicated rotations of the center of projection about [111].

versed. The effect is illustrated in Fig 9. Thus in the formal relationship developed, the pole figure shows a loss of the four-fold axis associated with cubic symmetry, but the planes of symmetry are preserved.

Coincidence Plot for a 22° Rotation

The nature of the relationship between the two highly preferred orientations involved suggests that a discrete mechanism operates in the formation of the "secondary" crystals. It has previously been shown that the primary unit of growth is probably a twin and that this unit forms in cubically aligned copper which has been observed to contain twins. This circumstance suggests that the twinned unit might be derived from a twin pair in the starting material by a mechanism which rotates the unit by a 22 or 38° rotation about the twinning pole. In order to attempt to gain an insight into the nature of the mechanism thereby suggested, it is useful to examine the relationship between the crystallographic orientations, before and after "secondary recrystallization." Referring to Fig 12, the small filled circles of net *A* represent the positions of the atoms in a (111) plane of the ideal cubic orientation. The large filled circles then represent the positions of the atoms in a neighboring layer. Net *B* is derived by a 22° rotation of the latter net (or a 38° rotation in the opposite direction) about an arbitrary point of this net. The positions of the open circles in the resulting net then represent the positions of the atoms of a (111) plane for the orientation after "recrystallization." This formal construction is not intended to imply that the orientation change actually occurs by means of the indicated rotational shear operation. Rather, it serves only to illustrate the relative positions of the atoms in a (111) plane before and after "secondary recrystallization."

However, examination of the figure reveals several striking features. It is seen that ¼ of the atoms of the new orientation are in coincidence with atoms of the old orientation, and the positions of these coincidence atoms define a unique equilateral net which is a multiple of the primitive net. Moreover, the remaining atoms can be brought onto the sites of the new net by a very simple movement of the order of ⅓ of an interatomic distance.

In order to effect a three dimensional change in orientation, formally speaking, it is necessary to consider neighboring layers. The corresponding coincidence sites for such a layer are shown by small annular rings in net *A*. Fig 13 shows the completed re-orientation in detail for two layers, and in one section for three layers. Coincidence sites in the second layer are defined by triangles in this figure. The remainder of the structure is derived by a repeated stacking of such groups of three.

Although it appears that the formal operations have produced a 22° rotation of the structure, such is not the case. Actually, study of the plots shows

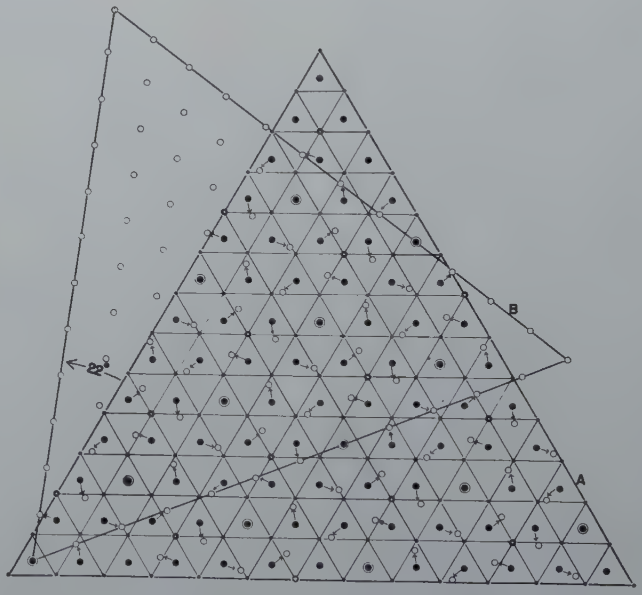

FIG 12—Coincidence plot showing relation between positions of atoms in an octahedral plane before and after a 22° rotation.

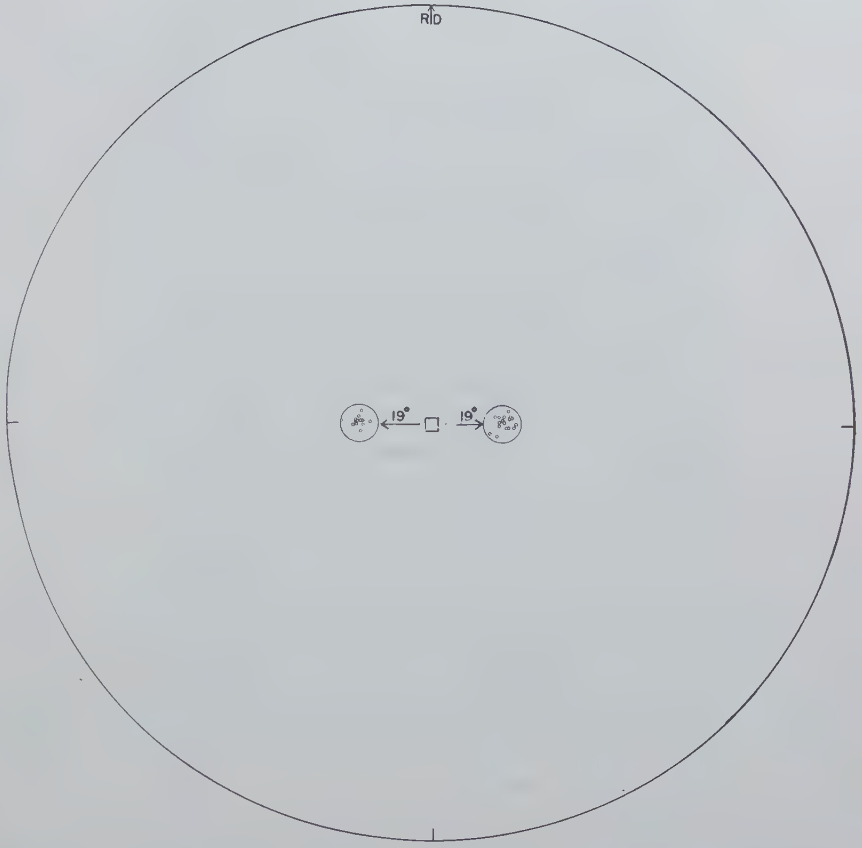

FIG 14—The positions of the central cube poles of 30 large crystals which are derived by rotation about [001].

the new orientation to be a twin of the starting orientation, rotated by 22°. Thus in the formal conversion of a twinned cubic crystal to the newly oriented twin, each part can be described as being related to its parent as a twin rotated 22°, or as its own orientation rotated 38° in the opposite direction.

Examination of the figure which shows the re-orientation for three layers reveals several interesting geometrical features. One sees that the coincidence positions uniquely define a multiple face-centered cubic lattice. All other original sites can be brought to their new positions by relatively short displacements.

A fundamental characteristic of the cluster of atoms composed of a coincidence atom plus its nearest neighbors is readily discerned. An atom in a cubic closest packed structure is surrounded by twelve nearest neighbors, six "around the waist" in any given (111) plane, three in the parallel plane above and three in the plane below—the latter six forming an octahedron about the central atom. For the case of twins, the packing of the three layers involving the composition plane and its contiguous neighbors corresponds to hexagonal closest packing. Thus, for a coincidence atom lying in the composition plane the atoms in the two sets of three nearest neighbors in adjacent planes define a triangular prism. Considering either case, in order to effect the formal orientation change under discussion, the six "waist" atoms all move in one direction, whereas the remaining two groups of three move in the opposite direction.

There are no obvious clues to a possible origin of the type (*b*) crystals which form most readily on slow heating. However, they exist with a very high degree of preferred orientation and there is a definite geometrical relationship between the atomic positions before and after "secondary recrystallizations." Fig 14 is a pole figure showing that the orientation can be related to that of the cubic by a ±19° rotation about a [100] axis parallel to the rolling direction. It is significant to note that the degree of preferred orientation is apparently considerably greater than that of the "cubic" material. Fig 15 illustrates the relative positions of the atoms before and after "recrystallization."

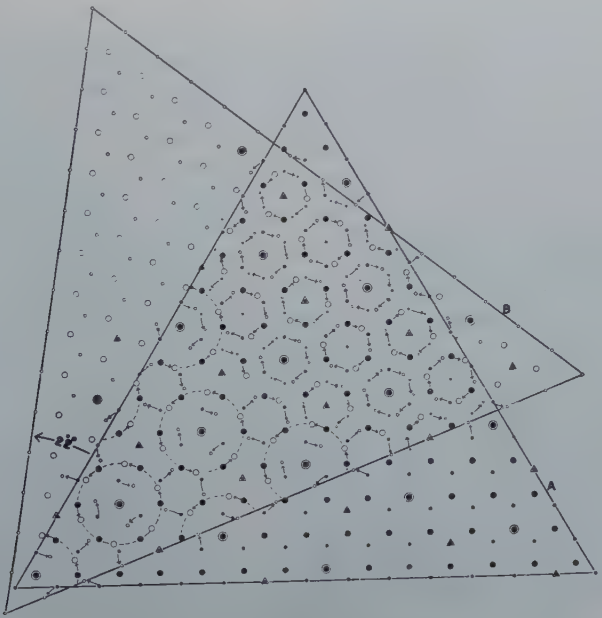

FIG 13—Coincidence plot showing relationship for two and three octahedral planes before and after a 22° rotation.

Observations on the Preparation and Annealing of Twin-free Cubically Aligned Copper

In order to test whether the occurrence of "secondary recrystallization" is dependent upon the presence of twins in the cubically aligned material, experiments were performed on apparently twin-free samples. It is known that the effect of a progressively diminishing grain size of the material prior to the heavy rolling reduction is the development of cubic material containing correspondingly diminishing amounts of twins.[16] Experiments in the current investigation have shown that, for starting grain sizes of the order of 0.01–0.1 mm, cubic material can be

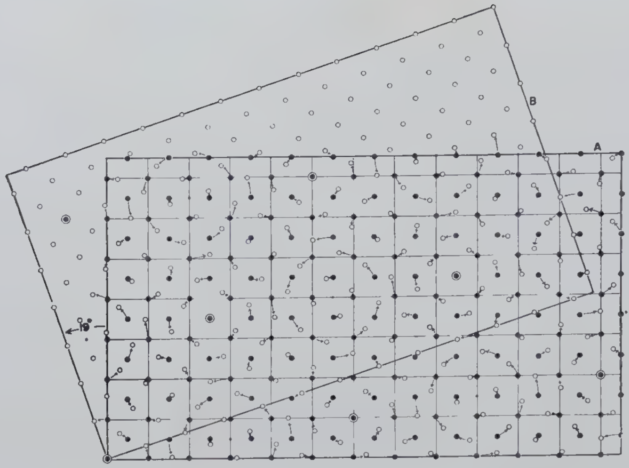

FIG 15—Coincidence plot showing relation between positions of atoms in a cube plane before and after a 19° rotation.

produced in which twins have not been detected by microscopic methods.

Starting with 0.5 mm grain size stock, samples of the finer grain size were produced by repeated cold forging and 300°C annealing treatments. Heavy cold rolling reductions and subsequent anneals were performed as described for the 0.5 mm material.

Fig 16 illustrates the kinds of samples obtained by rapid annealing to 1050°C. It is seen that all grains touch the edges of the sheet suggesting that growth has initiated at these boundaries. Careful examination of around 50 samples of the kind illustrated has shown that all the grains have this characteristic. Study of the microstructures of the sheared and torn edges of sheets annealed 1 hr at 850°C, a treatment which develops the structure existing just prior to "secondary recrystallization," revealed the presence of twinned cubically aligned grains along with other grains of varying orientations. By pickling the sheared edges of cold-rolled samples, regions where such grains might develop were removed and it was possible to obtain material apparently free of twins which did not undergo "secondary recrystallization" even during 6 hr anneals at 1050°C. Thus, twin-free cubically aligned copper does not undergo "secondary recrystallization" under the conditions of experimentation.

Fig 17 illustrates the microstructure of the twin-free material after a 6 hr anneal at 1050°C, and is to be compared with Fig 2, showing the microstructure of twin-bearing material after annealing at 850°C for 1 hr. Comparison shows that the grains persist in shapes characteristic of a nonequilibrium state of growth, displaying highly curved boundaries and varying angles between boundaries. The deviations from equilibrium shapes appear to be even more pronounced in the twin-free material. In this connection, it has been observed that the processing which develops the formation of twin-free material yields a markedly higher degree of preferred orientation than the processing which forms the twin-bearing material. Thus it would be expected that the former material would be the more sluggish in approaching the equilibrium state.

With regard to the sheets showing edge growth, an extensive study of the orientations of the large grains has not been made because of the lack of knowledge of the orientations existing at the cut and torn edges. However, the same kinds of orientations as were found in the twin-bearing material were also found in such samples, but with somewhat more spread in orientation. Several generations of twins were sometimes found in these grains. Also the type (*b*) rotations about a [100] pole are now found to occur about poles parallel to both the rolling and cross-rolling directions, and the relative abundance of these orientations is greater than for the grains arising in cubic material containing twins in the body of the sheet. Some additional orientations are occasionally encountered, but they have not been determined to date.

Fig 18 illustrates the shapes of grains grown by rapid annealing at 1000°C for 1 hr in a sample with edges sheared after the rolling reduction. It shows that growth of several crystals proceeded from the shorter edges at an approximately constant rate, thus meeting in the center of the sample. The large grains are all of the (*a*) and (*b*) types, as initially described.

Annealing at lower temperatures of the order of 850–900°C, a region in which the rates of growth are relatively slow, allows the development of characteristic shapes. Fig 19 illustrates the phenomenon, samples (*a*) and (*b*) having all edges sheared, and (*c*) and (*d*) having sheared edges parallel only to the cross-rolling direction. Again, all grains are of the (*a*) or (*b*) type in these samples, but some contain additional generations of twins. Unconsumed cubic material can be seen in the illustration. The existence of the characteristic shapes simply means that some planes are developed more readily than others. Previous investigators have ob-

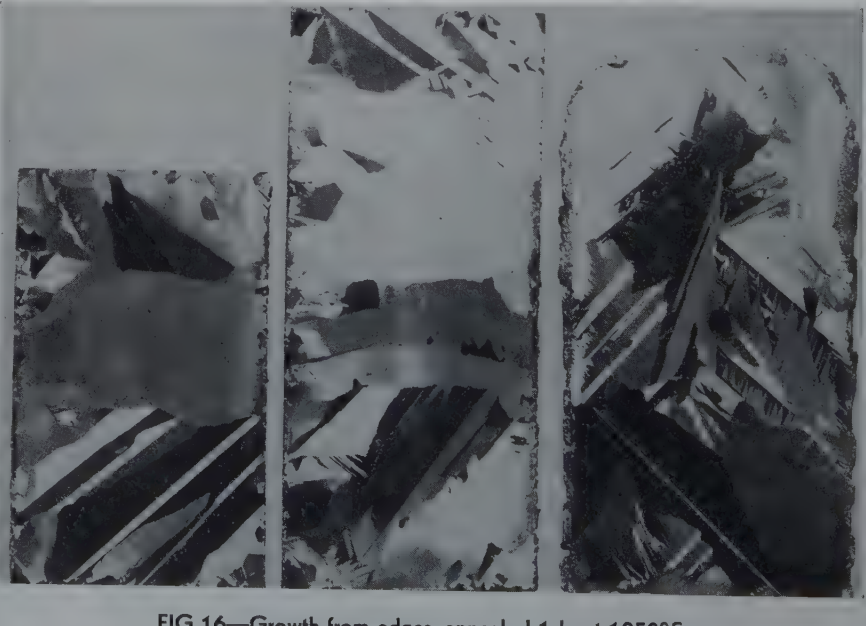

FIG 16—Growth from edges, annealed 1 hr at 1050°C.
Actual size.

served and described such typical shapes.[1-4,8]

It is important to note that elaborate lineage-like structures have been observed in the large grains. There has been no opportunity to study the nature of these structures, but it seems probable that they will afford additional clues to the dynamics of "secondary recrystallization."

The results of these experiments do not help particularly in determining whether the large grains grow in this kind of material from favorably oriented ones already existing at the edges, or by nucleation and growth of new ones in these regions. Nevertheless, the positive result that "secondary recrystallization" does not occur in twin-free cubically aligned copper, but does in twin-bearing material to form twinned units having orientations so discretely and simply related to the parent cubic orientation is the strongest kind of experimental evidence in favor of the concept of nucleation of new orientations at a twin boundary in the cubically aligned material.

On this basis, therefore, it would seem feasible to try to understand why a reorientation might occur at a twin boundary. The packing of layers in the face-centered cubic lattice follows the sequence: ABCABCABCABC . . . , corresponding to cubic closest packing whereas the sequence for a twinned crystal is: ABCABCBACBA . . . , in which there is a region of three layers corresponding to hexagonal closest packing: . . . BCB . . . Since copper does not crystallize in the hexagonal closest packed structure it can be concluded that the associated mode of packing is higher in energy content than that associated with cubic closest packing. There would, therefore, be an inherent tendency for the atoms to rearrange so as to eliminate the fault.

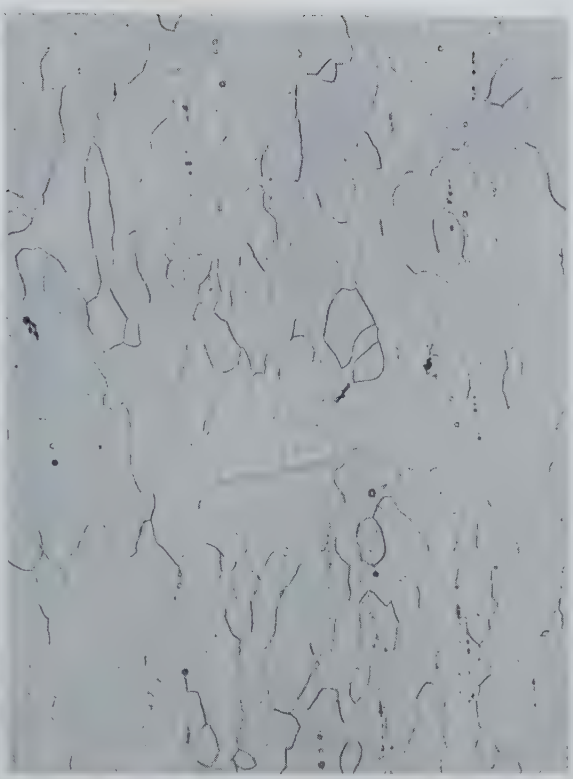

FIG 17—Structure of twin-free cubically aligned OFHC copper.
Starting grain size approx. 0.05 mm, rolled 98.5 pct, annealed 6 hr at 1050°C. Edges sheared and pickled before the anneal. 75 ×

Annealing Lightly Deformed Twin-free Cubically Aligned Copper

There is much current interest in the question of whether stacking faults are produced in face-centered cubic metals during deformation. For over twenty years, Mathewson has

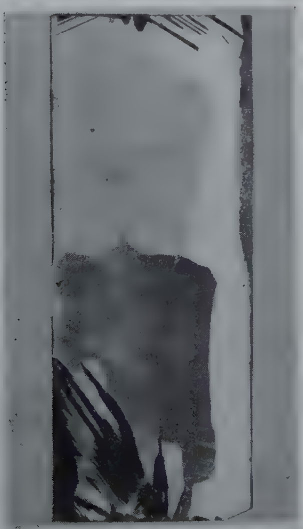

FIG 18—Growth from sheared edges, annealed 1 hr at 1000°C.
Actual size.

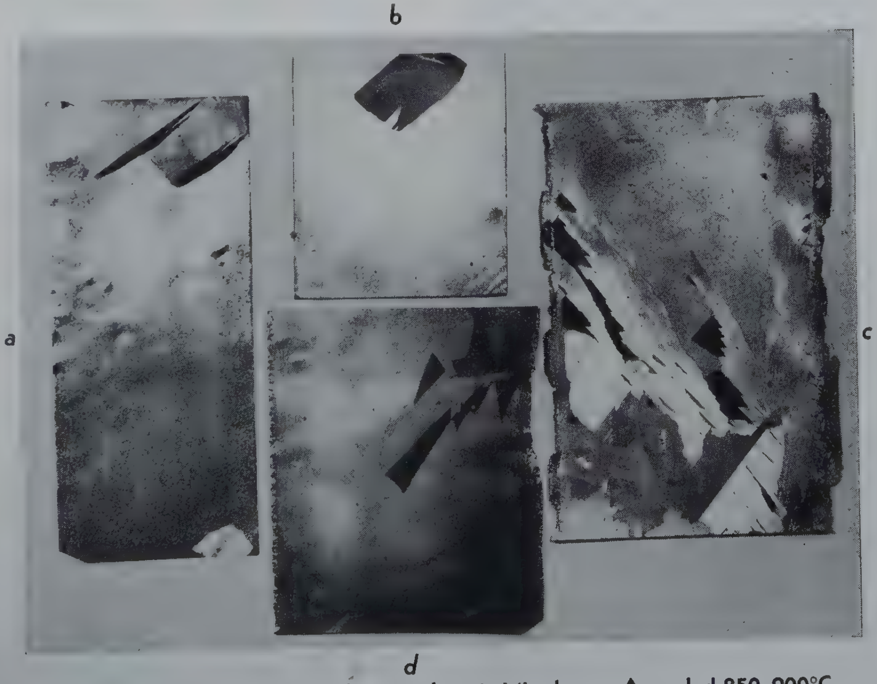

FIG 19—Growth from edges, showing characteristic shapes. Annealed 850–900°C.
a and *b*. All edges sheared. *c* and *d*. Edges parallel to cross-rolling direction sheared. Actual size.

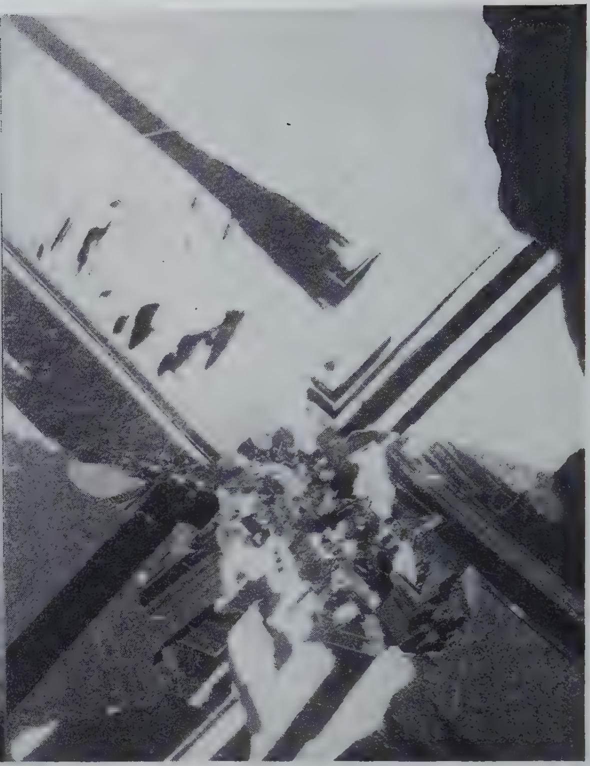

FIG 20 (left)—Deformation lines in peened twin-free cubically aligned copper.
75 ×.
FIG 21 (right)—Structure after peening and annealing.
10 ×.

held the view that annealing twins probably originate in copper during primary recrystallization from twins, or twin faults as he has more recently described them, arising within slip bands, during cold work,[9,10] and has presented experimental evidence showing that twins begin to form within slip bands during the annealing of worked copper. More recently Barrett has pointed out from structural considerations that twin faults might have nearly a 40 pct chance of forming during slip.[11] Thus, if twin faults can be induced in twin-free cubically aligned copper by cold work, it might be anticipated that primary recrystallization should produce twinned crystals of the same kind and orientation as are observed to form during "secondary recrystallization" in twin-bearing material. As a corrollary, the formation of these kinds of crystals could be taken as evidence for the formation of the faults during deformation. This interesting possibility has been subjected to a preliminary investigation by three techniques: peening, stretching, rolling.

Twin-free cubically aligned material was prepared from starting stock having a grain size of approximately 0.05 mm. Heavy rolling reductions were performed as already described, the edges of the resulting cold worked sheets were all sheared and pickled and the samples were then annealed for 1 hr at 1050°C. The microstructure of the kind of material thus formed has been illustrated by Fig 17.

A light ball peening produces copious deformation lines emanating from the peened spot and making approximately 45° angles with respect to the rolling direction, as shown by Fig 20. Recrystallization at temperatures as low as 600°C induces growth of twinned crystals in the regions of these markings, having twin directions at approximately 45° to the rolling direction and possessing orientations the same as those described for "secondary recrystallization." Orientations of type (*b*) are also found. Annealing at higher temperatures causes these grains formed by "primary recrystallization" to consume the remainder of the sample by grain growth. Fig 21 illustrates typical crystals formed during a 900°C anneal.

Annealing of samples containing deformation lines produced by tensile stretchings of the order of 5–10 pct yields the same kinds of results. Thus it is seen that both types of experiments are confirmatory and, in addition, show that the corresponding "primary recrystallization" occurs at temperatures several hundreds of degrees below those required for "secondary recrystallization" of unworked twin-bearing cubically aligned copper.

Light rolling reductions of the order of 1–5 pct yield similar effects as illustrated by Fig 22, except that in most samples the [111] rotations appear to be shifted from 22° toward a region around 30°, and the [100] rotations are shifted toward a region around 15° and now occur about the [100] pole that is normal to the sheet. The [111] poles of rotation and the central [100] poles of 18 large grains which grew on annealing lightly rolled twin-free cubically aligned copper are plotted in Fig 23. Presumably, the very close correspondence of the [111] poles to their "cubic" positions is simply a reflection of the very high degree of preferred orientation existing in the parent material.

The significance of this apparent change in the amount of rotation has not been evaluated. Perhaps the deformation process has caused the indicated additional rotation at the site of nucleation. On the other hand, coincidence plots very similar to those presented for the 22 and 38° rotations about [111] can be drawn for 28 and 32°, as shown by Fig 24, and a similar kind of plot can be constructed for [100] at 16°. Thus there is an alternative possibility that the reorientation of the rolled material proceeds according to the geometry of these new coincidence plots.

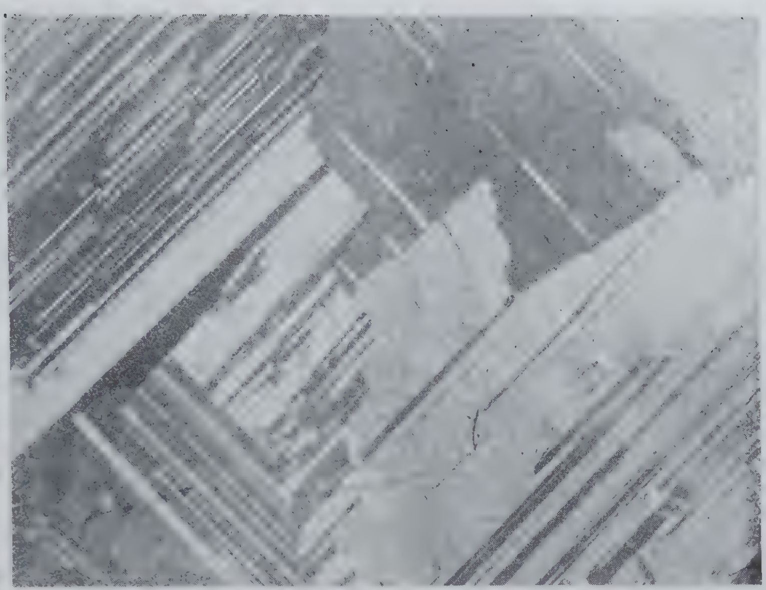

FIG 22—Structure after light rolling and annealing cubically aligned copper. 20 ×.

In this connection it is to be noted that in Fig 11 the spread is somewhat asymmetric, being greater in a clockwise direction. Thus, it is possible that a few of the orientations might be better described in terms of the 28 and 32° plots. An analysis based on considerably more data would be needed in order to evaluate properly this possibility.

Exploratory experiments on the recrystallization of more heavily rolled samples have revealed the very interesting finding that there is no pronounced change in the recrystallization orientation for deformations as high as approximately 35 pct, the limit of reduction that has been tried. It is interesting to note, in this connection, that Baldwin[12] has determined the orientation of 45 large grains produced by a 540°C anneal of cubically aligned copper that had been reduced 22 pct in thickness by rolling. He found a very high degree of preferred orientation which was described as:

Rolling Plane	Rolling Direction
($\bar{1}$13)	Between [110] and [301] 21° from [301]
($\bar{1}$13)	Between [301] and [2$\bar{1}$1] 10° from [301]

Examination of the data shows, however, that the orientation can also be described about as well by an approximately 30° rotation about [111].

On the other hand, the grain size decreases continuously as a function of increasing deformation, being of the order of ½ in. or more for a 5 pct reduction and approximately 1/32 in. for a 35 pct reduction. At the same time, the density of twins increases and the components become increasingly thinner, giving rise to a fine lamellar structure. It can be observed that growth in undeformed twin-free material (Fig 16, 18, and 19) produces a minimum number of twins, and therefore the suggestion arises that perhaps the formation of twins during growth in the deformed material might be associated with twin faults produced during the deformation.

The importance of the observation that the orientations of the grains resulting from the recrystallization of the rolled samples are essentially insensitive to the degree of rolling cannot be overemphasized, for it indicates the action of a fundamental, discrete mechanism of deformation and recrystallization throughout the range of deformation studied. An extensive study of the effects of deformation on the recrystallization orientations and structures is currently being prosecuted, and will be the basis of a separate, detailed publication.

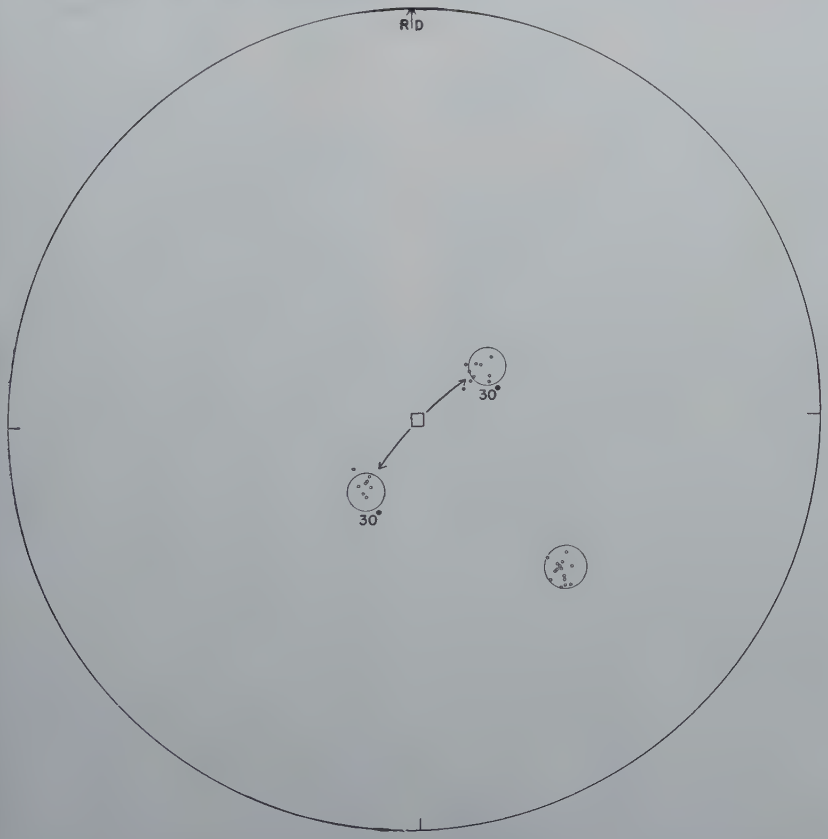

FIG 23—The positions of the octahedral poles of rotation and the central cube poles of 18 large crystals arising during annealing of lightly rolled cubically aligned copper. Centers of the ± 5° circles correspond to the 30° rotations about [111].

Considerations Concerning A Possible Mechanism

The considerable evidence in favor of a nucleation hypothesis warrants an investigation of a possible mechanism for "secondary recrystallization." Indeed, the final acceptance or rejection of such an idea may well depend on the outcome of a detailed analysis of the energetics of such a process. The experimental data and the geometrical relationships derived therefrom are of a suitable form to allow such an investigation. If it can be proven that nucleation cannot occur, then one is left with the apparent conclusion that reorientation occurs by the highly selective growth of constituents present in amounts too small to be detected. As a beginning, it seems that the following kinds of information should be given attention.

The lowest energy state of an assemblage of atoms in the solid state is a single crystal, and thus the polycrystalline cubically aligned material containing twins is naturally proceeding in the direction of this ideal state when it converts into huge single crystals. Grain boundaries are removed and therefore would be the most probable source of the driving energy required for the change. On the other hand, there is a change in orientation altering the geometrical distribution of atoms exposed at the surface of the specimen and, if this lowers the surface tension, the corresponding decrease in energy would likewise contribute to the driving force. The fact that the conversion occurs only if twin boundaries are present indicates that the energy associated with the stacking fault existing at a twin boundary is probably involved in the activation energy, in part at least. Experiments indicating that growth initiates at a surface, where the atoms have the greatest freedom of movement and are correspondingly more energetic, can be interpreted to mean that the associated surface energy likewise probably contributes to the activation energy. Other likely contributions could come from the localized statistical fluctuations in the distribution of thermal energy among the various atoms, and the distortional energy of imperfections such as vacant sites, foreign atoms, and others.

A reasonable picture, therefore, would have the most favored site of nucleation be the region of intersection between a grain boundary, a twin boundary and the surface. A necessary condition to the atomic reorganization occurring during nucleation would be the disappearance of the grain boundary region involved. A disordered area would therefore vanish and the corresponding imperfections would be discharged at the surface. Experimental observations indicate that the twin boundary would be maintained, but would be reoriented.

It is important to point out that a structurally perfect twinned crystal would not be expected to undergo recrystallization, even though the region of the boundary is a place of higher energy than the remainder of the interior of the crystal, for this energy is locked up for a perfect crystal. Thus it is necessary to evaluate the interaction of structural imperfections, such as vacant sites or the disorganization associated with a grain boundary, with this faulted region. The balance of forces normally maintaining the atoms in their faulted positions would be upset by the entry of imperfections into the boundary region, and might therefore promote the initiation of an atomic rearrangement in accord with the inherent tendency to de-twin or remove the fault. Indeed, inspection of Fig 12 and 13 shows that the nearest three atoms to a coincidence site in the plane above and in the plane below it actually travel in the directions of de-twinning sites in the formal picture, but achieve the equilibrium positions corresponding to the observed reorientation by moving only somewhat more than one-half the distance to a normal de-twinning site. Thus in this picture the reorientation might be described as the end product of an abortive attempt to de-twin.

It is interesting to note that the r.m.s. value of the amplitude of the thermal vibration of the atoms at the temperatures of the re-arrangement is roughly 0.3Å, which corresponds to approximately ⅓ the total distance of formal travel between sites. Statistical fluctuations are considerable and become more pronounced with increasing temperatures. Thus, it would be desirable to evaluate the probability that an atom, or perhaps a few atoms, in cooperation with an imperfection such as a vacant site, might spontaneously execute oscillations favoring the initiation of the rearrangement.

Presumably, a critical number of atoms would have to reorient in accord with the formal cooperative movements indicated by the coincidence plots of Fig 12 and 13 in order to form a stable nucleus. Once this critical size is reached, the remaining atoms in the crystal involved in the nucleation would reorient rapidly by cooperative movements. Further increase in size would be achieved by boundary migration, and presumably would proceed readily because of the favorable orientation relationship.

It seems reasonable that the induction period observed for isothermal recrystallization might, in part at least, be essentially a reflection of the improbability of the nucleation event. Accordingly, few nuclei would form, and huge grains would consequently be developed. The observation that the grain size decreases with increased heating rate might be interpreted as follows. The probability that a nucleus will form at any given temperature depends on the time the sample is held at that temperature. Thus, on slow heating one nucleus might form at a relatively low temperature and consume the entire sample before another nucleation event could occur. On rapid heating, there would not be as great a probability for nucleation to occur at so low a temperature. Rather, initial nucleation would occur more probably at a higher temperature. Since the frequency of nucleation will increase with temperature as a result of the increased amplitude of thermal vibration the overall result would be the formation of many grains.

The significance of the experimental observation of specific directions of rotation about the individual [111] poles has not been evaluated, but is apparently an important clue to an understanding of the structural nature of the reorientation phenomenon.

In the very important case of the recrystallization of the lightly deformed samples of cubic material, there is no difficulty in understanding the nature of the driving force. It is the residual energy of cold work. Although its structural nature is not too well understood, it is quite possible that a deeper insight might result from continued studies of recrystallization utilizing the concepts of atomic rearrangement as revealed in the studies of "secondary recrystallization."

General Application of Coincidence Plots to Secondary Recrystallization

None of the orientations observed during the current investigation has corresponded with those described by either Dahl and Pawlek[1] or Cook and Richards.[2] However, the orientation study of the latter team was on material prepared by a rolling reduction of 85 pct, and it is known that such a reduction is insufficient to promote the kind of "secondary recrystallization" studied in the current investigation.

Bowles and Boas[3] have reported rotations of approximately 30° about [111] on the basis of a study of 11 large grains produced in their experiments. Examination of the method of analysis employed in the evaluation of their data shows that the 30° figure results from an averaging process of all observed rotations. It seems that re-evaluation of the data might show it to fit the 22 and 38° regions reported in the current study.

One element in common with nearly all the reported observations of new orientations produced by "secondary recrystallization" in cubically aligned metals and alloys is that old and new orientations are related by rotations about [111] and [100] axes. It would seem feasible to attempt to evaluate the significance of the variety of recorded observations utilizing the variety of possible coincidence plots, although it is to be emphasized that very carefully acquired and analyzed data will be needed. For [111], there are plots corresponding to 28, 22, 18, 15, 13, 11½°, etc., but there are no experiments indicating rotations other than the two discussed. For those values less than about 15°, the density of coincidence sites is relatively low and the corresponding plots can probably be ignored. For [100], there are plots corresponding to 37, 28, 22½, 19, 16, 14, 12½°, etc. A commonly reported rotation for both copper and 50:50 nickel-iron alloys is approximately 30°,[4] and there is one report[13] of 37–38° for a 30:70 nickel-iron alloy, a coincidence plot for which is shown in Fig 25.

Some Implications of the Concept of Coincidence Plots

In applying the concepts of atomic rearrangement suggested by the experiments on "secondary recrystallization" to the experiments on lightly deformed cubically aligned copper, the deformation was considered as a means for inducing faults locally comparable in structure to twin boundaries. Nevertheless, the reorientation on annealing is fundamentally primary recrystallization and suggests that this approach may be a good tool for the study of both deformation and primary recrystallization. If extensive orientational relationships of the nature described by coincidence plots are found between deformed and recrystallized grains, they will provide strong evidence in support of the suggested atomic rearrangements; and detailed studies of recrystallization orientations accordingly should make it possible to learn more about the fine structure of deformed metal. The fruitfulness of this field of investigation is indicated by some observations which appear to be consistent with the present concept. Further research will be necessary to evaluate them.

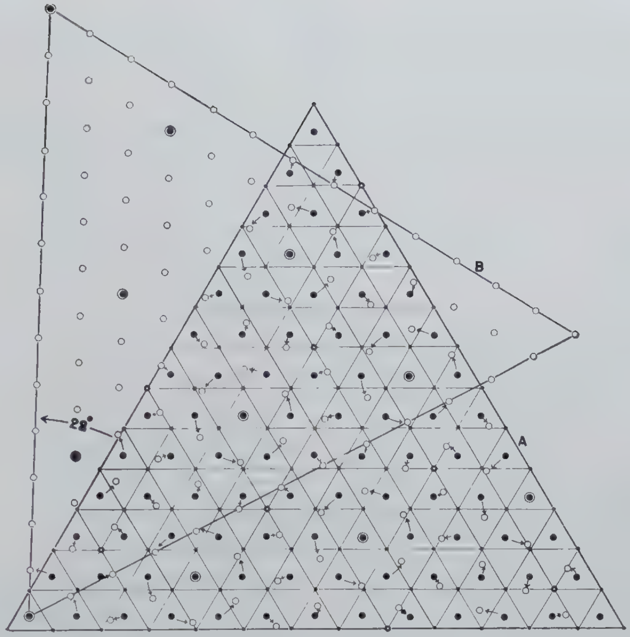

FIG 24—Coincidence plot showing relation between positions of atoms in an octahedral plane before and after a 28° rotation.

Although the structure of aluminum is based on the face centered cubic lattice it is well known that annealing twins are rarely formed by this metal. Thus, it can be predicted that a modified picture of the deformation and recrystallization processes, as developed for copper, should result from similar studies on cubically aligned aluminum. Exploratory experiments have shown that twin-free cubically aligned "high-purity" aluminum does not undergo "secondary recrystallization" on annealing in air at 650°C for 24 hr. On the other hand, recrystallization of lightly rolled samples produces the same kinds of orientations as observed for twin-bearing copper after "secondary recrystallization," with both types of orientations, (*a*) and (*b*), being found. Twinned crystals are almost entirely absent, and the rotations about [111] are predominantly of the 38° type.

In this connection, it is interesting to note that Barrett[17] has observed clusters of orientations of new grains produced by the recrystallization of deformed single crystals of aluminum, compressed so as to avoid the formation of deformation bands. The orientations of these clusters can be related with considerable success to the deformation orientations by approximately 38° rotations about the [111] poles.

It was pointed out by Cook and Richards[14] that components of the (100)[112] rolling deformation texture of brass are related to components of the so-called (113)[112] recrystallization texture by a 30° rotation about a [111] pole near the rolling direction. It is possible to reproduce the pole figure, referred to as (113)[112] quite well by a 22° rotation in one direction and a 38° rotation in the other around the same [111] poles of a single component of the deformation texture. This would, of course, also be true of any of the other metals having the same textures. Rotations may occur also in wires which have a [111] fiber axis and recrystallize to the same fiber texture, as copper and aluminum are reported to do—although the rotation of each crystal would be definite in amount and the random distribution around the axis would arise from the randomness of distribution in the deformation structure. Moreover, triangular coincidence plots of the basal plane of hexagonal close packed metals would be similar to those illustrated for the octahedral planes of the face centered cubic lattice, and similar rotations might be expected. Thus, the retention of the [00.1] axis normal to the plane of the sheet during recrystallization of heavily rolled hexagonal close packed metals is comparable to retention of the [111] fiber axis in wires of face centered cubic metals. Likewise, worked material of random orientation could retain the randomness on recrystallization if each grain undergoes a rotation during the recrystallization. Although the "cubic" texture, having no complements, is considerably simpler than the deformation texture from which it arises, there is a component of deformation texture which is related to "cubic" by a 38° rotation about [111].

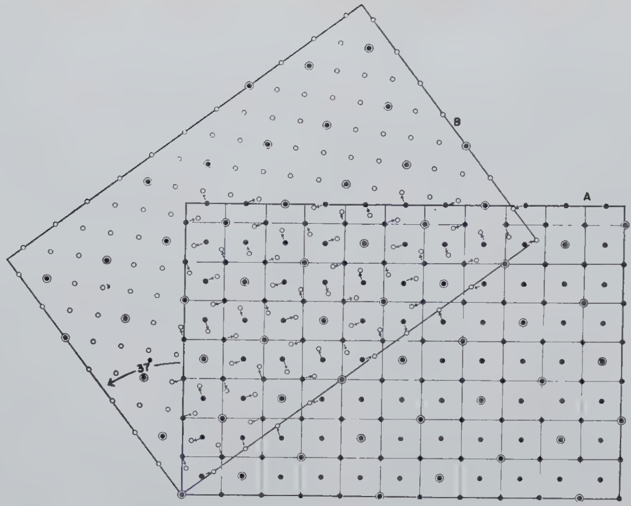

FIG 25—Coincidence plot showing relation between positions of atoms in a cube plane before and after a 37° rotation.

The conversion of the so-called (113)[112] low temperature recrystallization texture of brass to (110)[112] at higher temperatures[15] may be a form of "secondary recrystallization" without the development of very large grains. This reversion to the deformation texture could be accomplished by a reversal of the rotations occurring during primary recrystallization.

Dunn has observed clusters of orientations of recrystallized grains formed on annealing lightly deformed iron-silicon crystals,[18–19] and it would be pertinent to determine whether these new orientations can be related to the deformation orientations by means of coincidence plot relations. One might anticipate coincidence relationships on (110) planes, since they are the most densely packed ones in the body centered cubic lattice.

Summary

A formal relationship between pairs of orientations, which can explain extensive apparent rotations of a structure in terms of short, cooperative atomic movements, has evolved from a study of the orientations of the large grains that can be produced during the "secondary recrystallization" of twin-bearing cubically aligned copper. Experimental evidence indicates that the large grains are formed by a process of nucleation and growth of new orientations, with nucleation apparently initiating at twin boundaries. Two types of orientations are found. Each can be related formally to the ideal cubic orientation by rotations about [111] and [100] poles, respectively. The former always contains twins at approximately 45° to the rolling direction. There are simple relationships between the relative positions of the atoms before and after "secondary recrystallization," which indicate that the reorientation probably occurs by a cooperative movement of atoms.

Twin-free cubically aligned copper, when lightly deformed by peening or tensile elongation, recrystallizes to form grains of the same kinds and orientations as are produced by "secondary recrystallization" of unworked twin-bearing cubically aligned copper. This result supports the hypothesis that twin faults form during the deformation, and participate in the recrystallization of the worked material to form annealing twins.*

Some speculative comments are made concerning a possible mechanism of "secondary recrystallization," pointing out the need for a theoretical analysis, and emphasizing the apparent necessity of considering imperfections in searching for the driving and activation forces. The driving force is probably mainly the energy associated with the disorganization existing at a grain boundary, but the differential in surface energy between the orientations before and after reorientation must be considered in addition. The activation energy is probably associated with a combination of the energies corresponding to the stacking fault existing at a twin boundary, imperfections such as vacant sites, the localized fluctuations of thermal energy amongst the various atoms, and the relatively loose binding of surface atoms.

A detailed account is given of the observations made on the preparation and annealing of cubically aligned copper, and a description is given of the sizes, shapes and orientations of grains formed by "secondary recrystallization."

Some implications of the results of the "secondary recrystallization" studies are discussed as they might be related to recrystallization phenomena in general.

Acknowledgments

Acknowledgment is made to the American Brass Co. for permission to publish; to Mr. John R. Freeman, Jr., Technical Manager, whose interest and support made the work possible; and to Mr. E. W. Palmer, in charge of the Copper Research Laboratory, for sponsoring the work and for his critical advice and encouragement. The staffs of the laboratories of the Company deserve much credit for assistance throughout the project.

Before the paper was written, various aspects of the experimental results were discussed with Professors P. Debye, J. D. H. Donnay, and C. H. Mathewson. We wish to thank these gentlemen for their kindly and stimulating consideration.

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* By private communication, Dr. Robert Maddin of the Hammond Laboratory of Yale University informs us of some particularly timely results of his current work on the tensile elongation and subsequent annealing of single crystals of alpha brass. After recrystallization, twinned crystals are found whose orientations can be related to the parent orientation by opposing rotations of approximately 22 and 38° about a [111] pole.

Kinetics of the Reactions of Zirconium with O_2, N_2 and H_2

EARL A. GULBRANSEN* and KENNETH F. ANDREW*

Introduction

The gas-metal reactions of zirconium are very interesting. The metal is extremely stable at room temperature to reactions with the several gases present in air and the metal will stay bright indefinitely. However, at temperatures of several hundred degrees higher the metal reacts readily with oxygen, nitrogen and hydrogen. This behavior, in addition to the fact that zirconium is one of the higher melting point metals which might have high temperature applications under the proper conditions, resulted in the work reported in this communication.

There are several factors which indicate that zirconium might have good oxidation resistance at elevated temperatures. These are: (1) the high melting point of approximately 1860°C, (2) the high melting point of the oxide of approximately 2675°C, (3) the high degree of thermodynamic stability of the oxide to chemical reaction and the low decomposition pressure of the oxide and (4) the possible formation of a continuous oxide film since the volume ratio of oxide to metal is greater than unity. The unfavorable factors are: (1) the metal reacts to form nitrides, hydrides and carbides, (2) the oxide is soluble at elevated temperatures in the metal and (3) the oxide ZrO_2 undergoes crystal structure transformations at high temperature.

The oxidation resistance of this metal is not only a question of the rate of film formation but is complicated by the fact that the oxide and other reaction products dissolve in the metal which in turn will affect the physical and mechanical properties of the metal.

The protection of the metal to nitride formation must be considered separately from the oxide problem. One unfavorable factor is that the volume ratio of the nitride to the metal is about unity. This indicates that a discontinuous film might be formed. This paper will present measurements on the rates of reaction of the metal with O_2, H_2 and N_2 over a wide temperature and pressure range. The reaction in high vacuum and the stability of the several compounds formed will be presented. The results are correlated with fundamental rate theory and with the physical and chemical structure of the metal and film.

Literature

Although many papers have been published on the chemical reactions of zirconium with various gases, comparatively few are concerned with the protective nature of the metal and its reactions at normal pressures. The studies in the pressure range below 0.01 mm of Hg gas pressure are largely of interest in the nature of the adsorption of gases by hot filaments in high vacuum apparatus. The reactions of zirconium in this pressure range have been reviewed by Fast[8] and by Raynor.[27] In spite of certain differences of opinion as to the maximum adsorption temperatures for various gases, the low pressure range is qualitatively understood. Some of these papers will be mentioned briefly here.

1. LOW PRESSURE

Ehrke and Slack[7] find that oxygen reacts above 885°C and hydrogen above 760°C. Nitrogen does not react up to a temperature of 1527°C. Fast[9] on the other hand observes that oxygen is absorbed above 700°C and nitrogen at temperatures exceeding 1000°C. Hydrogen is absorbed from 300° to 400°C and liberated between 500° and 800°C. It is readsorbed at 862°C and released above 862°C.

Hukagawa and Nambo[22] find a rather complicated picture for the absorption of oxygen. A rapid initial absorption is found between 180° to 230°C. Further oxygen is not taken up until a temperature of 450°C is reached. The optimum temperature for complete absorption is 650° to 700°C. Nitrogen is found to be completely adsorbed at 600°C. However some of the gas is evolved at higher temperatures. Their data on the absorption of hydrogen indicate some of the gas is removed at 550°C.

Guldner and Wooten[17] in a study of the low pressure reactions of zirconium with various gases observed that the reaction with oxygen occurs at temperatures above 400°C and that the oxide is formed. The reactions with carbon monoxide and carbon dioxide occur rapidly at temperatures of about 800°C with the oxide and carbide being formed. Zirconium reacts at temperatures of 400°C slowly and at 800°C rapidly to form the nitride and with hydrogen and water at 300°C to form the hydride and a mixture of the oxide and hydride respectively.

2. NORMAL PRESSURE

DeBoer and Fast[3] in a study of the electrolysis of oxygen in zirconium find that the metal absorbs up to 40 at. pct of oxygen without forming a new phase. The solubility of nitrogen in the lattice has been studied by de Boer and Fast[4] and Fast[10] and is found to be considerable. At higher temperatures the oxide dissolves in the lattice at an appreciable rate according to Fast[10] and the zirconium surface becomes active.

De Boer and Fast[4] and Hägg[18] have studied the solubility of hydrogen and find that at room temperature the solubility corresponds to $ZrH_{1.95}$. Desorption occurs on lowering the pressure. Hydrogen is stated to be more soluble in the β-form and the

Cleveland Meeting, October 1949.
TP 2659 E. Discussion of this paper (2 copies) may be sent to *Transactions* AIME before December 1, 1949. Manuscript received December 15, 1948; revision received April 18, 1949.

* Westinghouse Research Laboratories, East Pittsburgh, Pa.

[8] References are at the end of the paper.

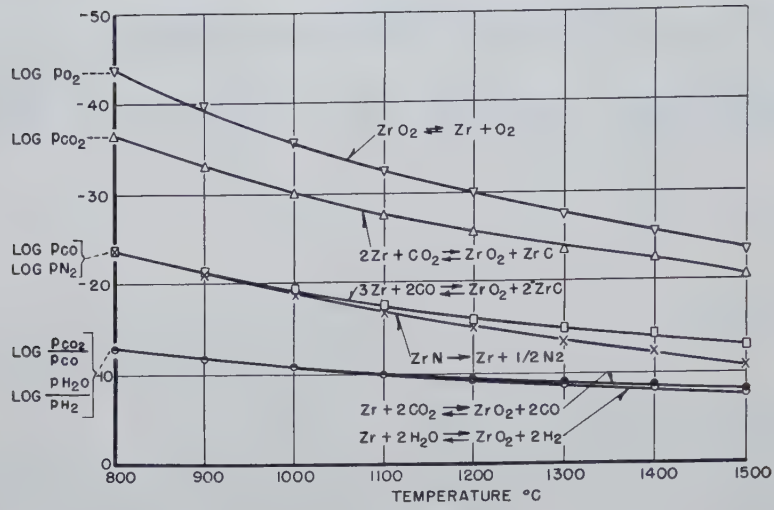

FIG 1—Equilibrium calculations on Zr reactions.

transition between the α and β forms occurs at 865°C.

Hall, Martin and Rees[19] have studied the solubility of hydrogen in zirconium and Zr-O solid solutions at temperatures up to 1000°C and at pressures of 1 to 760 mm of Hg. The hydrogen desorbed on lowering the pressure.

3. CRYSTAL STRUCTURE

The crystal structures of the oxide films formed on zirconium at temperatures from 300° to 600°C using the electron diffraction method have been studied by Hickman and Gulbransen.[21] The monoclinic form of ZrO_2 was observed over the temperature range. ZrO_2 is reported to exist in at least three crystalline modifications: monoclinic,[20] cubic[5] and tetragonal[28] from X ray diffraction studies. Kelley and coworkers[23] from a specific heat study of the oxide ZrO_2 have shown the existence of an (α) and a (β) form with a transition at 1205°C.

Zirconium forms a nitride ZrN having a cubic lattice of the sodium chloride type.[2] The reaction with hydrogen has been studied by Hägg.[18] Several phases are observed. Hydrogen is adsorbed up to 5 pct in the hexagonal close packed lattice without an appreciable change in lattice parameters. The lattice constants of the solid solutions of oxygen and nitrogen have been given by Fast.[8]

4. STABILITY

The stability of the several oxides of zirconium has been studied by Cohn and Tolksdorf.[5] They found the monoclinic modification to be stable to 1000°C and the tetragonal modification above 1000°C. The latter may be cooled to room temperature. After long heating above 1900°C a trigonal modification was found to form. When cooled a transition occurs at 625°C.

5. EQUILIBRIUM CALCULATIONS ON THE REACTION OF ZIRCONIUM WITH SEVERAL GASES

Zirconium reacts with most of the common gases to form stable compounds with the exception of the inert gases. The chemical equilibrium of these reactions may be evaluated for reactions in which the end products are ZrO_2, ZrN or ZrC. Data are not available on the reaction with hydrogen.

The following reactions of zirconium with O_2, H_2O, CO_2, CO and N_2 can be evaluated from thermodynamic data:

1. $Zr(s) + O_2(g) \rightleftarrows ZrO_2(s)$
2. $2\ Zr(s) + CO_2(g)$
   $\rightleftarrows ZrO_2(s) + ZrC(s)$
3. $3\ Zr(s) + 2\ CO(g)$
   $\rightleftarrows ZrO_2(s) + 2\ ZrC(s)$
4. $Zr(s) + \frac{1}{2}\ N_2(g)$
   $\rightleftarrows ZrN(s)$
5. $Zr(s) + 2\ CO_2(g)$
   $\rightleftarrows ZrO_2(s) + 2\ CO(g)$
6. $Zr(s) + 2\ H_2O(g)$
   $\rightleftarrows ZrO_2(s) + 2\ H_2(g)$

The letters (s) and (g) refer to the solid and gaseous states respectively.

The free energy of formation of ZrO_2 (α) and ZrO_2 (β) is calculated from the data given by Thompson[31] and using the recent data of the Pacific Experiment Station of the Bureau of Mines[23] on the entropy of ZrO_2 (α) and the heat content of ZrO_2 (α) and ZrO_2 (β). The free energy of formation of ZrC is calculated from an equation given by Kelley.[23] This equation is open to some question and may involve a maximum error of ±2 in the logarithm of the pressures calculated for the reactions in which ZrC is involved. The results of the calculations are shown in Fig 1. The logarithm of the gas pressure or pressure ratios are plotted against the temperature in °C for the several reactions.

The results show the following: (1) ZrO_2, ZrN and ZrC are stable at all temperatures shown in the graph and zirconium from a thermodynamic point of view will remove O_2, N_2, CO and CO_2 at the lowest pressures used in modern vacuum technology, (2) the reactions of water and carbon dioxide to form the oxide and hydrogen and carbon monoxide respectively are possible below 1100°C in vacua of the order of 10^{-7} mm of Hg.

Apparatus

BALANCE

The microbalance with its auxiliary apparatus is similar to that previously described.[12,13] The sensitivity of the balance is 0.86 divisions (0.001 cm) per microgram and the weight change can be estimated to 0.3×10^{-6} g. The balance zero point is constant and the instrument is insensitive to pressure and to small changes in the temperature of the surroundings.

VACUUM SYSTEM

The vacuum system has been changed from that previously described.[12] The length of the glass tubing connecting the several parts of the apparatus has been decreased and the diameter increased to a minimum of one inch. In addition, a high speed single jet mercury diffusion pump of the Illinois design has been added to increase the pumping speed at the outlet of the pumps by a factor of ten. The Illinois pump is backed by a two jet Princeton type of mercury diffusion pump and a Cenco Hyvac fore pump. No grease, wax, cement or metal seals are used in the system.

FURNACE TUBES

Previous to this work we have used pyrex, Vycor and quartz tubing for the construction of the furnace vessel. For higher temperatures and better vacuum conditions we have recently found synthetic mullite or zircon to be very valuable materials for the construction of furnace vessels. These materials are vacuum tight when properly made and can be sealed directly to pyrex. This feature allows double walled furnace vessels to be constructed in which the outer tube serves as a protecting vacuum.

McLeod gauge pressures of 10^{-6} mm or lower can be achieved with these vessels at temperatures of 1175°C and perhaps higher. Leak rate measurements with the McLeod gauge on these furnace tubes show values as low as 1.4×10^{-9} mm liters per sec. after pumping over night at 900°C. We do not infer that such readings represent conditions in the furnace vessel itself since a cold trap is used on the system.

The determination of the pressure in the furnace tube is a difficult problem and any apparatus for such a task must be incorporated in the tube itself. This problem will be discussed in a later communication. For chemical and metallurgical purposes the chemical reactivity of the furnace atmosphere is of more importance than the absolute value of the pressure. This can be measured by observing the reaction rate of an active metal such as zirconium in the furnace tube itself.

GAS PURIFICATION

The purification of the oxygen and hydrogen are the same as previously described.[12] The nitrogen is purified by passing the tank gas over hot copper turnings at 400°C and removing water vapor by passing over $Ba(ClO_4)_2$. The gas is next passed over palladium asbestos at 400°C and then through another column of $Ba(ClO_4)_2$ and ascarite. It is finally passed over a liquid nitrogen trap at 0.1 atmosphere pressure.

SAMPLES

The specimens of zirconium are cut from a five mil sheet of the metal obtained from the Foote Mineral Co. No accurate analytical data are available on the material. However, the supplier states that it contains approximately 3.0 pct hafnium and about 0.04 pct iron. We are indebted to Mr. W. C. Lilliendahl of our Bloomfield Works for furnishing additional information on the presence of carbon, nitrogen and oxygen in zirconium samples. Several samples of 0.05 in. drawn wire have shown the following analysis: carbon 0.01–0.05 pct; nitrogen 0.01 pct; and oxygen 0.02–0.04 pct.

The specimens weigh 0.6840 g and have a surface area of about 15 cm². Most of the samples were abraded starting with No. 1 grit and finishing with 4/0 paper. The last stage of the abrading is carried out under purified kerosene.

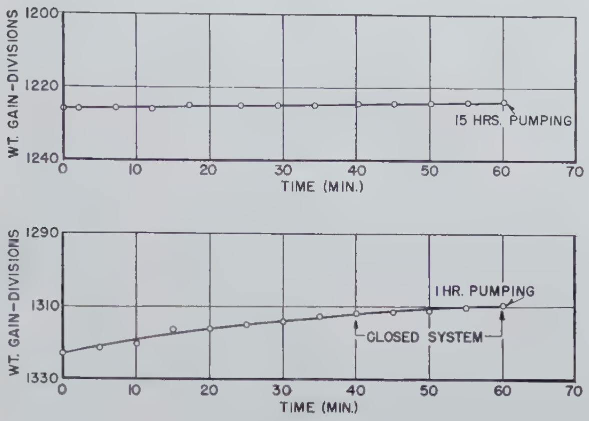

FIG 2—Reaction Zr in vacua-zircon furnace tube 900°C.

Results and Discussion

HIGH VACUUM REACTION

A consideration of the high vacuum reactions of the metal under investigation is essential if a film free metal is desired at the start of the experiment. For most metals this can be achieved by heating the metal to the reaction temperature in a vacuum of the order of 10^{-6} mm of Hg and then reducing the film initially present with pure hydrogen.

The problem of preparing and keeping an active metal such as zirconium in a film free condition is practically impossible. Zirconium not only acts as a getter but the oxide ZrO_2 is not reduced by hydrogen or other reducing gases. Since the oxide is soluble in the metal at high temperatures, the oxide film may be removed by heating. However, on cooling, a film will again form in the vacuum. This procedure results also in the addition of oxide and other impurities to the metal.

Since the oxides are not reducible we have adopted the use of abraded specimens. Every effort is made to keep the films formed during abrasion to a minimum. On heating the specimen in vacuum to the reaction temperature an additional film forms. With many metals this film is only several atomic layers thick. However, zirconium forms an unprotective film and the film forms continuously in the best vacuums that we have been able to obtain.

It is of interest to show the extent of the vacuum reaction of zirconium in a furnace tube made from zircon or mullite. The furnace tube consists of two concentric tubes closed at one end and sealed at the other end to pyrex. The space between the concentric tubes is evacuated. Fig 2 shows the results of heating a zirconium specimen. The weight gain is given in scale divisions (1 division = 1.2 micrograms). Two curves are shown for a temperature of 900°C and for a McLeod gauge pressure of 1×10^{-6} mm of Hg or lower. The weight gain of a sample of zirconium suspended in the furnace tube is plotted against the time in minutes. The first curve shows the reaction rate after one hour of pumping time. A reaction rate of 0.2 divisions per min. is observed. This corresponds to 0.016 micrograms per cm² per min. or about 1Å of ZrO_2 per min. assuming a surface roughness ratio of unity. The second curve shows the reaction rate after 15 hr of pumping. A reaction rate of 0.04 divisions per min. is observed which corresponds to 0.0032 micrograms per cm² per min. or 0.2Å per min. The calculations on thickness are based on the assumption that the film is composed largely of ZrO_2.

We are interested also in the nature of the reaction at temperatures below 425°C and for practical pumping times of up to one hour. These are the conditions that we use in our rate studies. Experiments indicate that the maximum film formation observed is of the order of 0.70 micrograms per cm² for one hour of reaction at 425°C. If this is assumed to be ZrO_2, a maximum thickness of 43Å may be formed. In most of our measurements the vacuum formed film will be a fraction of this value.

REACTION WITH OXYGEN

The reaction is studied as a function of the time, temperature, pressure and surface treatment. The results are presented in Fig 3, 4, 5, 6 and 7. The weight gain in micrograms per cm² is plotted against the time in minutes.

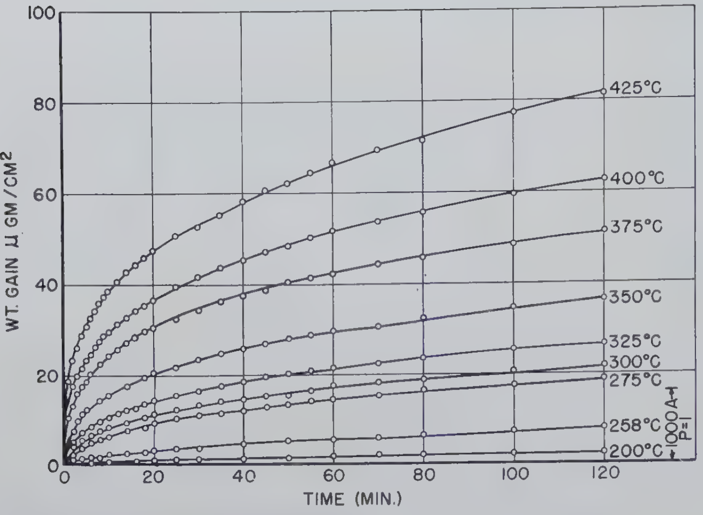

FIG 3—Reaction Zr with O_2 7.6 cm. Effect of temperature 200–425°.

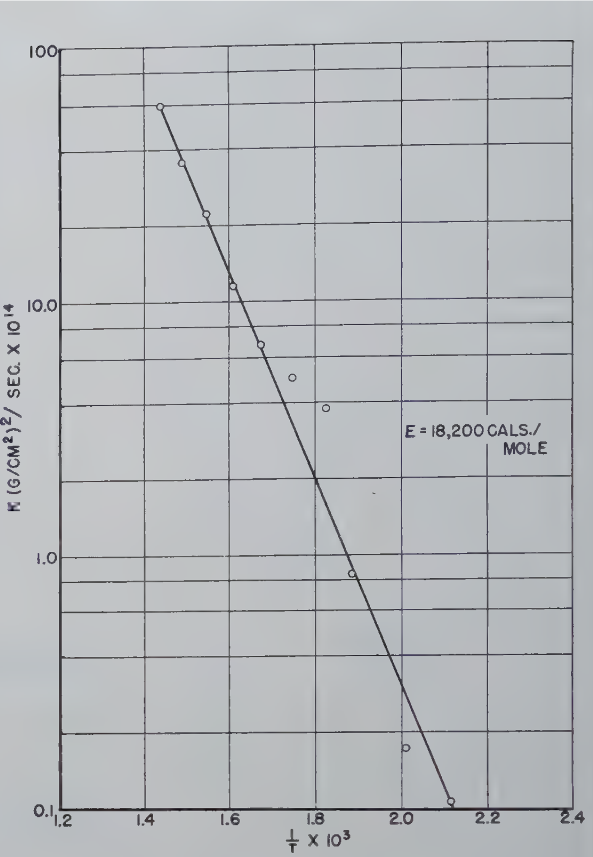

FIG 4—Reaction Zr with O_2 7.6 cm. Parabolic rate constant vs. 1/T.

Assuming the ratio of real area to measured area to be unity ($P = 1$) and the oxide film to be ZrO_2,[21] the thickness of the oxide film in Angstroms is 61.5 times the weight gain in micrograms per cm². Unless specifically mentioned the samples are abraded.

Time

Several experiments are made at 7.6 cm pressure and at 375°C to check the method and the reproducibility of the surface preparation. The results on the oxygen reaction can be duplicated within several percent. One run is extended for 7 hr but no additional information is obtained over the 2 hr experiments.

The shapes of the oxidation curves are similar to those observed for other metals.[15] A fast reaction rate is observed in the early stages of the reaction which gradually decreases as the film thickens. In this sense the oxide film may be said to have protective properties.

Time and Temperature

Fig 3 shows the effect of temperature on the reaction for the range of 200° to 425°C. At the right of the curves is shown the weight gain corresponding to a thickness of 1000Å. A comparison of the 200°C curve with the 425°C curve after 2 hr of reaction shows a film thickness of 150Å at 200°C and a thickness of 5000Å at 425°C.

Time and Temperature Equations

Three equations have been used to explain the time variation of the oxidation rate. The parabolic rate law was first derived by Pilling and Bedworth[26] on the basis of diffusion of oxygen through the oxide lattice. It has been derived more recently by Wagner and Grünewald[33] and by Mott.[24] The equation is

$$W^2 = Kt + C$$

Here W is the weight gain, t is the time and K and C are constants. Mott[25] has recently modified the parabolic law to account for the presence of a potential due to oxygen ions on the surface. The field resulting from this potential is greatest for thin films and becomes small for thick films.

The logarithmic rate law has been derived by Tammann and Köster.[30] This equation states that

$$t = \beta\,(e^{W/\alpha} - 1)$$

Here α and β are constants. The physical basis for this rate law has not been well established although Wagner[34] has recently derived the law from physical considerations.

The linear rate law is given by the equation

$$W = Kt + C$$

This equation states that the reaction rate is independent of film thickness and the limiting factor in the reaction rate is not a simple diffusion mechanism.

Dunn[6] first applied the Arrhenius equation to the temperature coefficient of oxidation rate measurements. The Arrhenius equation as applied here states that

$$K = Ae^{Q/RT}$$

Here K is the parabolic reaction rate constant, Q the activation energy and A is a constant.

Mott[24] has considered the physical interpretation of Q for the case where ions and electrons are diffusing through the oxide to react with oxygen at the gas interface.

One of the authors[16] has applied the transition state theory of chemical reactions and diffusion processes as developed by Eyring and coworkers[11] to the oxidation reaction. The parabolic rate law constant K is given by the following equation:

$$K = \frac{2kT}{h}\lambda^2 e^{\Delta S^*/R} e^{-E/RT}$$

Here ΔS^* is the entropy of activation and E the energy of activation. λ is the interatomic distance between diffusional states, k is Boltzman's constant and h is Planck's constant. This equation is useful since both ΔS^* and E can be calculated. ΔS^* is the probability or steric factor of the particular barrier limiting the reaction.

Table 1 . . . Parabolic Rate Constants and Diffusion Constants, Entropies, Energies and Free Energies of Activation, for the Oxidation Process

t°C	K, cm² per sec	D_0, cm² per sec.	ΔS^* Cal per mol per °C	E Cal per mol	$-T\Delta S^*$ Cal per mol	ΔF^* Cal per mol
200	0.0391×10^{-14}	4.92×10^{-8}	−24.6	18,200	11,650	29,850
225	0.0633×10^{-14}	3.10×10^{-8}	−25.6	18,200	12,750	30,950
258	0.311×10^{-14}	4.94×10^{-8}	−24.8	18,200	13,200	31,400
275	1.413×10^{-14}	12.6×10^{-8}	−23.1	18,200	12,660	30,860
300	1.87×10^{-14}	8.35×10^{-8}	−24.0	18,200	13,750	31,950
325	2.50×10^{-14}	5.6×10^{-8}	−24.8	18,200	14,800	33,000
350	4.28×10^{-14}	5.3×10^{-8}	−25.1	18,200	15,600	33,800
375	8.26×10^{-14}	5.7×10^{-8}	−25.0	18,200	16,200	34,400
400	13.20×10^{-14}	5.36×10^{-8}	−25.2	18,200	17,000	35,200
425	22.15×10^{-14}	5.55×10^{-8}	−25.2	18,200	17,600	35,800

Table 2 . . . Summary of Data Temperature Effect

t°C	T°K	$\frac{1}{T} \times 10^3$	$\frac{dW}{dt}$ (micrograms per cm² per min) $P = 7.6$ cm O_2					
			At the Following Thicknesses (micrograms per cm²)					
			10	20	30	40	50	60
300	573	1.7542	0.280					
325	578	1.6722	0.445	0.113				
350	623	1.6051	1.46	0.345	0.156			
375	648	1.5432		1.10	0.459	0.173	0.125	0.0782
400	673	1.4859		1.79	1.03	0.382	0.272	0.179
425	698	1.4327		5.91	1.97	1.08	0.555	0.418

Time and Temperature Correlation

The applicability of the parabolic and logarithmic rate laws can be tested by plotting the square of the weight gain against time in the former case and the weight gain against the logarithm of the time in the latter case. A straight line would show that the law is obeyed.

Parabolic plots are made of the data. Although some deviations are observed from a straight line during the initial stages of the reaction, there appears a trend to approach a straight line for the longer periods of the reaction.

Plots of the weight gain against the logarithm of the time show smooth curves of increasing slope. The logarithmic rate law does not apply for this reaction over the complete time and temperature range studied.

The linear rate law is not found to fit the data as can be seen by an examination of Fig 3.

It is necessary to conclude that none of the simple rate laws suggested adequately explains the data. The modification of the parabolic rate law as suggested by Mott is useful since it predicts the sign of the deviation as well as the general shape. However, the theory has not been developed in sufficient detail to apply to the data.

Temperature Dependence

The temperature coefficient of the reaction rate is a very useful quantity to evaluate. If the reaction rate can be related to a mechanism an energy of activation may be calculated for the process. If the theory or mechanism is unknown it is possible to show the thickness or time dependence of the temperature coefficient. Assuming that one mechanism has a constant temperature coefficient it may be possible to show whether one or more than one mechanism is responsible for the reaction. We will use both points of view in the discussion that follows.

1. *Energy and Entropy of Activation.* Fig 4 shows the parabolic rate law constant K plotted against $\frac{1}{T}$. The temperature range is from 200°–425°C. The limiting slopes at long times are used where the data deviate in the earlier stages of the reaction from the straight line.

The energy of activation of the rate determining process is calculated from the plot. A value of 18,200 cal per mol is found. The temperature independent factor $e^{\Delta S^*/R}$ is calculated from the parabolic rate law constant as expressed by the transition state theory. The equations for the parabolic rate law constant K and the diffusion constant D_0 are as follows

$$K = \frac{2kT}{h} \lambda^2 e^{\Delta S^*/R} e^{-E/RT}$$

$$D_0 = \frac{K}{2e^{-E/RT}}$$

The significance of the terms has been previously discussed. The parabolic rate law constants vary from 0.0391×10^{-14} cm² per sec at 200°C to 22.15×10^{-14} cm² per sec at 425°C. In terms of Angstroms of film thickness, the above rates correspond to 2 Å per sec at 200°C to 50 Å per sec at 425°C.

Table 1 shows the values for the parabolic rate law constants and diffusion constants and the entropies, energies and free energies of activation of the rate determining process. The K values are connected to thickness by the use of the density of the oxide and the stoichiometric ratio of oxygen in the oxide. A surface roughness ratio P of 1 is assumed.

The energy of activation 18,200 cal per mol is lower than that observed for several other metals previously studied. The entropies of activation are negative and are close to those observed for the oxidation reactions on iron and aluminum. ΔS^* is a measure of the (frequency factor) or the probability of an ion with a definite energy getting through the lattice. For most metals ΔS^* is negative although tungsten and molybdenum show positive values. The free energy of activation is made up of the energy of activation E and the term $T\Delta S^*$. The sign and magnitude of the term $T\Delta S^*$ thus determines whether the effective barrier ΔF^* is increased or decreased by the steric factor. The values of ΔF^* for the oxidation of zirconium vary from 29,850 to 35,800 cal per mol. These are somewhat lower than those observed for other metals at 400°C, for example, the ΔF^* for the oxidation of zirconium is 35,200 cal per mol while the following values are obtained for iron, tungsten, molybdenum and aluminum respectively: 39,150, 37,700, 36,260 and 39,900 cal per mol.

2. *Temperature Coefficient as a Function of Film Thickness:* The data shown in Fig 3 are plotted on a large scale and a smooth curve drawn through the points. The slopes of these curves $\frac{dW}{dt}$ are determined for film thicknesses of 10, 20, 30, 40, 50 and 60 micrograms per cm² by Lagrange's formula for determining slopes at a given point. These slopes are tabulated in Table 2 at the same film thickness as a function of the temperature. Fig 5 shows the slopes plotted on a logarithmic graph as a function of $\frac{1}{T}$. A series of straight lines of approximately the same slope are observed. This result indicates an approximately constant temperature coefficient over a wide thickness range. This suggests that one mechanism may be responsible for the reaction.

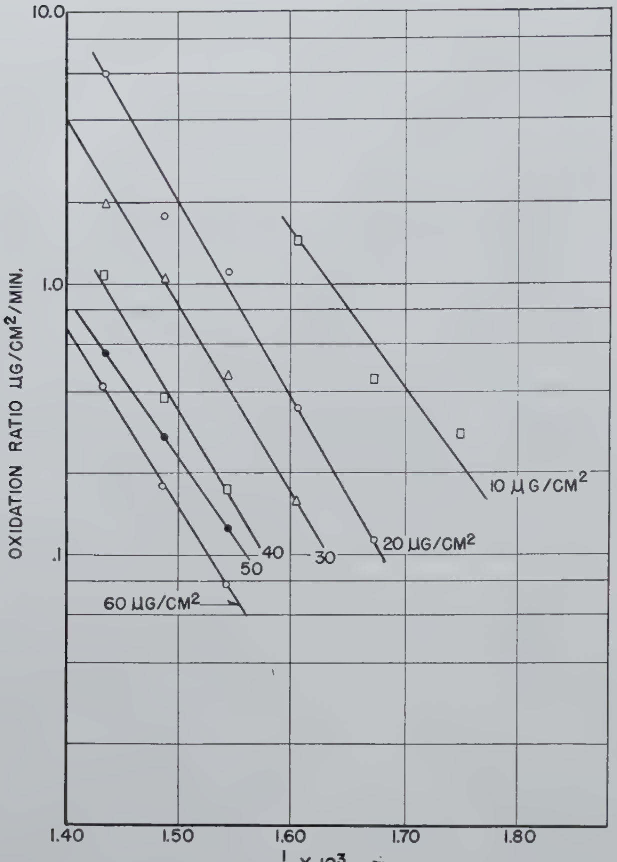

FIG 5—Oxidation rate vs. temperature at film thickness of 10–60-g per cm².

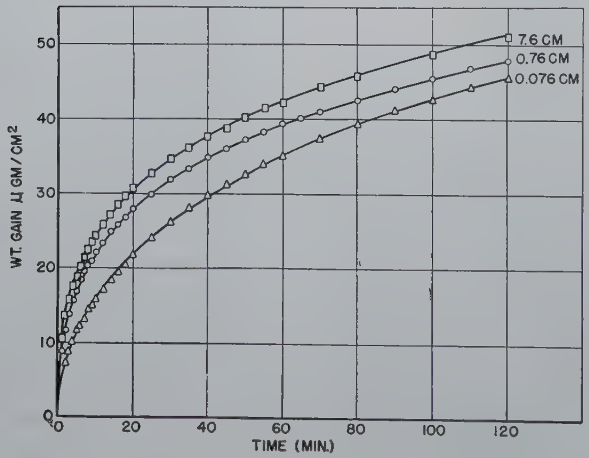

FIG 6—Reaction Zr with O_2 375°C. Effect of pressure.

Pressure Effect

The effect of pressure on the reaction at 375°C is shown in Table 3 and in Fig 6. The pressure is varied by a factor of 100 from 7.6 cm to 0.076 cm of oxygen. The effect is largest for the thin film range and decreases with increasing film thickness. No simple relationship with the pressure has been determined.

Effect of Abrasion

Fig 7 shows a comparison of the reaction of an abraded sample and an unabraded sample. The abraded sample oxidizes more rapidly than the unabraded sample. The effect may be related to one or more of the following factors: (1) increased surface area, (2) removal of initial oxide film, and (3) change in the size and state of the surface crystals.

REACTION WITH NITROGEN

Table 3 . . . Summary of Data Pressure Effect

Pressure Atmospheres	$\frac{dW}{dt}$ (micrograms per cm² per min) T = 375°C At the Following Thicknesses (Micrograms per cm²)				
	0	10	20	30	40
0.1	15.9	5.35	1.1	0.46	0.24
0.01	14.1	3.33	1.02	0.35	0.17
0.001	8.6	1.36	0.82	0.31	0.20

In this section the reactions of zirconium with purified lamp grade of nitrogen are studied in detail as a function of time, temperature and pressure and a comparison of two gas sources is used to show the strong effect of impurities. The results are shown in Fig 8–11 and discussed in the following subsections. In all of the figures the weight gain in micrograms per cm² is plotted against the time and where necessary the temperature is given at the top of the graph.

1. *Purity of Nitrogen:* A study of the reaction of nitrogen with zirconium presented the problem of obtaining a sufficiently pure gas to make the reaction with impurities a small part of the nitrogen reaction. To show this effect we can compare the results of the reaction using purified commercial nitrogen and purified lamp grade of nitrogen. The time course of the reaction of the purified commercial nitrogen at 350°C is identical with the reaction using the purified lamp grade of nitrogen at 700°C.

Mass spectrometer analysis of the gases showed the presence of 0.3 pct oxygen in the commercial gas source before purification. The lamp grade of nitrogen shows 0.01 pct. The gas analyses are not complete since hydrogen is not determined at low concentrations by our mass spectrometer.

It is of interest to note that colored films are formed using the purified commercial nitrogen while no films are observed in the experiments at the higher temperatures using the purified lamp grade of nitrogen. Electron diffraction studies show the outer layers of the colored films to be the monoclinic form of ZrO_2 while no diffraction patterns were obtainable with the higher temperature experiments using lamp grade of nitrogen. We do not conclude that no oxide or hydride is formed with the purified lamp grade of nitrogen but rather that the reaction rate is so slow that one has to use a higher temperature to observe an appreciable reaction. The temperatures used in the nitride study are in general above the decomposition temperature of the hydride. At temperatures above 500°C both the nitride and oxide appear to be soluble in the metal and colored films would not be expected to be observed.

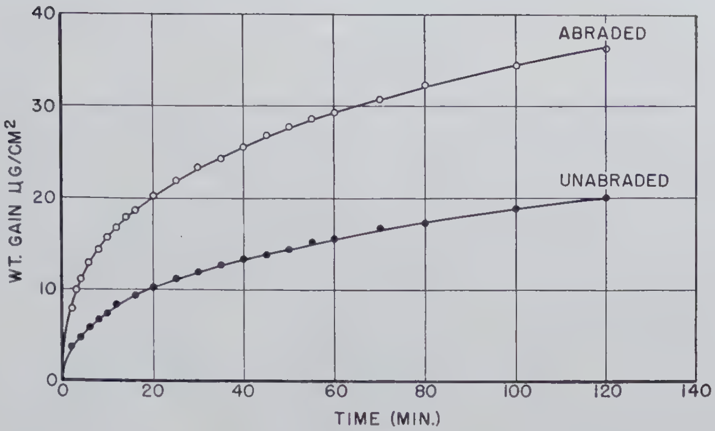

FIG 7—Reaction Zr with O_2 350°C. Effect of abrasion.

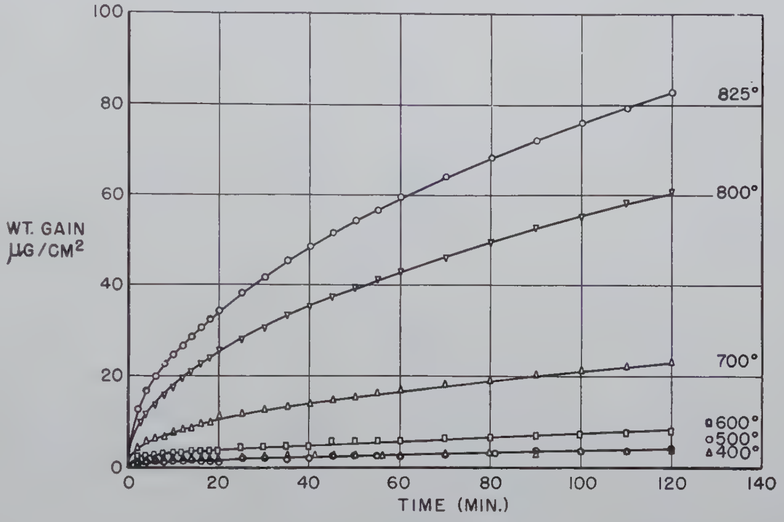

FIG 8—Reaction Zr with pure N_2—7.6 cm. Effect of temperature.

The stability of the nitride to vacua of the order of 10^{-6} mm of Hg has been tested experimentally. The reaction products formed with purified nitrogen at 750°C are stable to temperatures of at least 900°C. However, if the reaction products formed with purified commercial nitrogen at 425°C are heated, part of the product decomposes at 490°C. This may indicate the presence of a nitride of low stability or a hydride. The decomposition of the hydride occurs at about this temperature.

These experiments show: (1) that impurities of oxygen and hydrogen are very important in determining the rate of reaction and (2) that purified lamp grade of nitrogen is a rather pure source of nitrogen.

2. *Time and Temperature:* The time behavior of the nitride reaction for several temperatures from 400° to 825°C is shown in Fig 8. In all of the experiments the reaction rate decreases as the film thickens. The effect of temperature on the reaction rate is quite uniform.

The shape of the weight gain curves indicates that a parabolic rate law may agree empirically with the data. Fig 9 shows a plot of the weight gain squared against the time for the nitriding reaction at 750°C. The agreement is very good even for very small amounts of reaction. The agreement with the parabolic law at other temperatures is tested and except for the 400° and 500°C experiments is found to be good. At the lower temperatures deviations are observed for the initial stages of the reaction.

Although the data may obey the parabolic rate law the mechanism of the reaction may be quite different from the oxidation reaction since the nitride is soluble in the metal at these temperatures.

If we consider that the diffusion of ionic species through the surface film and surface interface reactions is not limiting the reaction it is possible to apply the results of diffusion theory to the reaction.

Van Liempt[32] has considered the problem of the degassing of metals and he has by the aid of an approximation method obtained a solution to the problem. His equation is

$$Q/Q_0 = \frac{8}{d}\sqrt{\frac{Dt}{\pi}}$$

Here Q is the quantity of gas evolved or taken up at any time t, Q_0 is the original quantity of gas in the metal and D is the diffusion coefficient. This expression can be reduced to the parabolic law,

$$W/W_0 = K\sqrt{t}$$

In the van Liempt expression the only term that depends upon the temperature is D. Since the data fit the parabolic rate law it is of interest to evaluate the temperature dependence and relate this to the energy of activation E for the diffusion process.

Table 4 shows the values of the parabolic rate law constants for the temperature range of 400° to 825°C. Fig 10 shows a logarithmic plot of the parabolic rate law constant against $\frac{1}{T}$. A straight line is found for the temperature range of 600° to 825°C. Below 600°C the data fall away from a straight line. An energy of activation of 39,200 cal per mol is calculated.

Table 4 . . . Reaction Zirconium with Nitrogen 7.6 Cm

Parabolic Rate Law Constants

t°C	T°K	$1/T \times 10^3$	K(g per cm^2)^2 per sec
400	673	1.4859	2.082×10^{-15}
500	773	1.2935	1.835×10^{-15}
600	873	1.1453	7.77×10^{-15}
700	973	1.0276	6.85×10^{-14}
750	1023	0.9774	1.90×10^{-13}
800	1073	0.9319	5.13×10^{-13}
825	1098	0.9107	9.60×10^{-13}

3. *Pressure:* Fig 11 shows the effect of pressure on the time course of reaction with purified lamp grade nitrogen at a temperature of 750°C. The rate of reaction is nearly independent of the pressure in the range of 7.6 cm to 0.15 cm pressure. This evidence indicates that mechanism of reaction is very different from what is observed in the reaction with hydrogen which is presented in Fig 14 and discussed in the section *Reaction with Hydrogen* of this paper. In the case of hydrogen it is shown that the reaction rate is proportional to the square root of the pressure at a given temperature.

Barrer[1] has summarized several systematic studies of the permeation of hydrogen through metals. Two possible

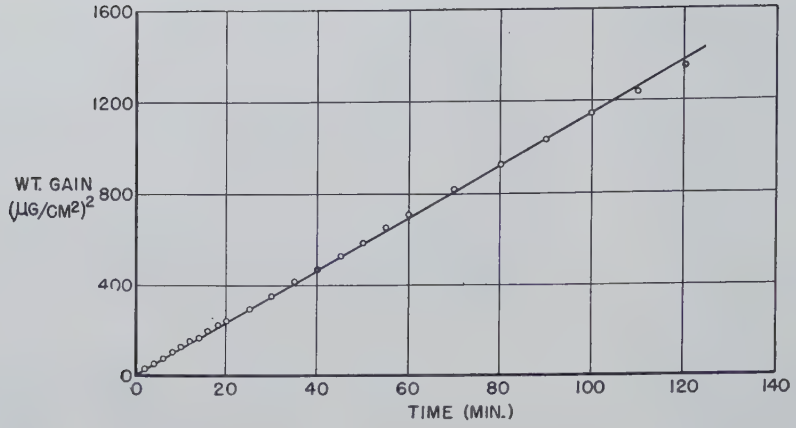

FIG 9—Reaction Zr with pure N_2—7.6 cm. Parabolic plot.

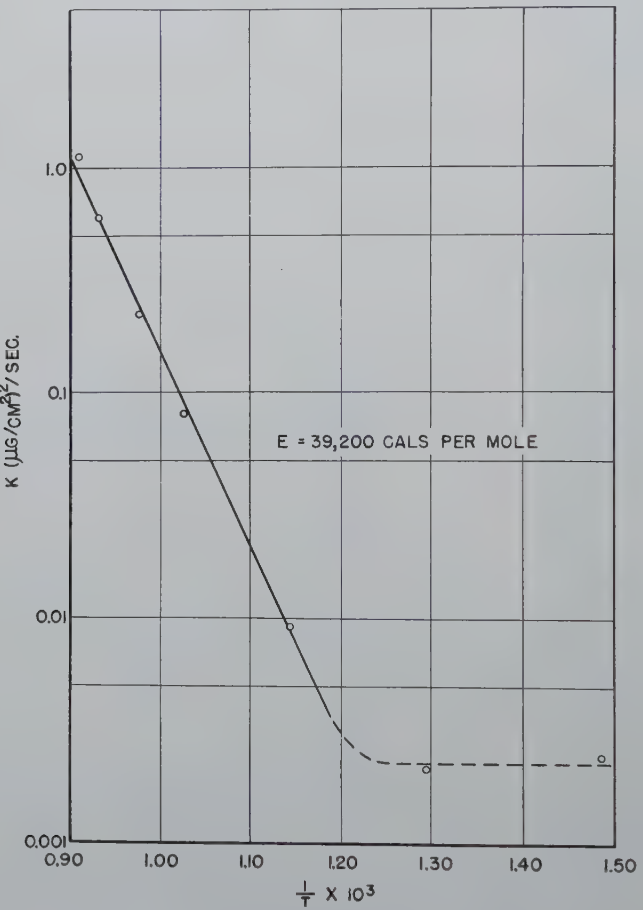

FIG 10—Reaction Zr with pure N_2—log K vs. $\frac{1}{T}$.

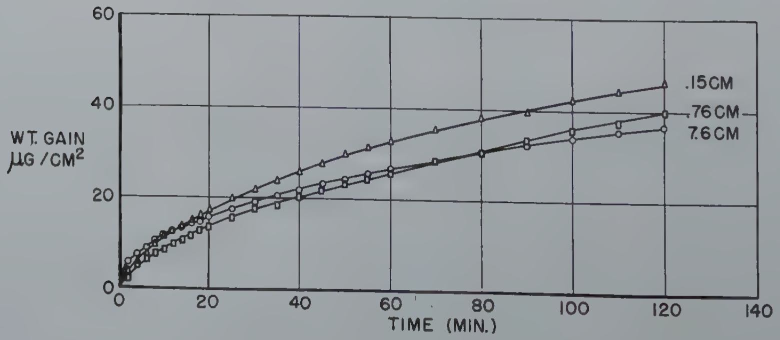

FIG 11—Reaction Zr with pure N_2—Effect of pressure.

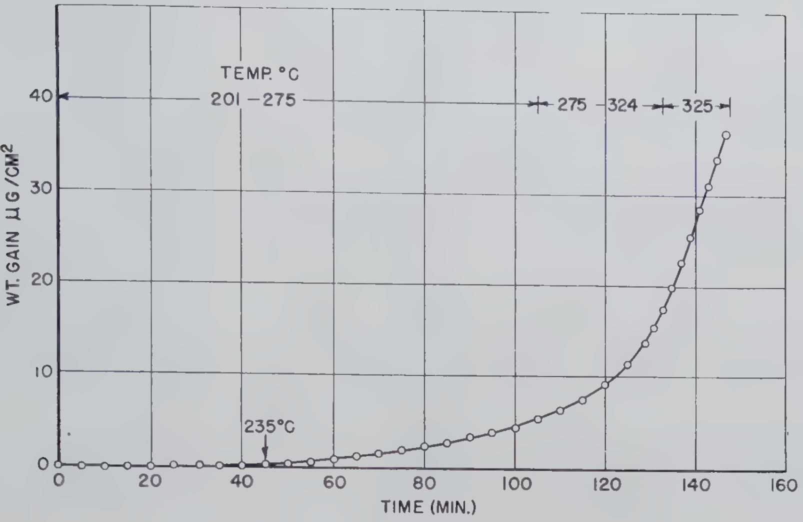

FIG 12—Reaction Zr with H_2 2.2 cm 201°–326°C.

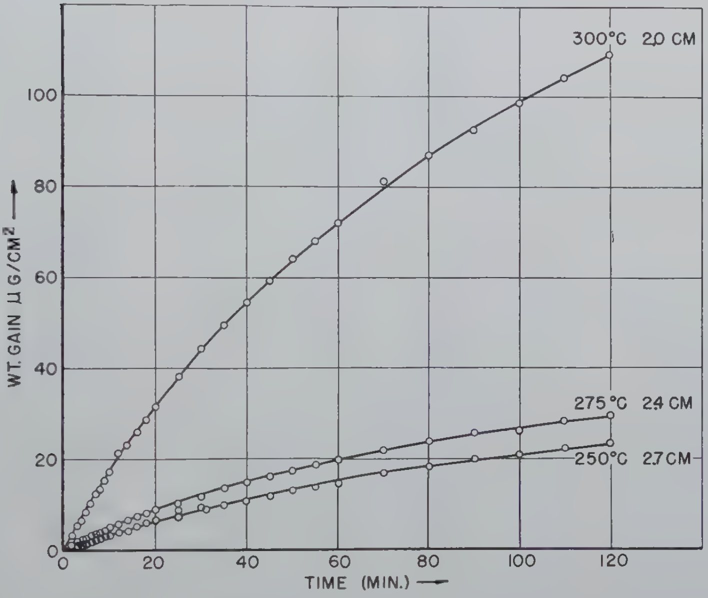

FIG 13—Reaction r with H_2. Effect of temperature.

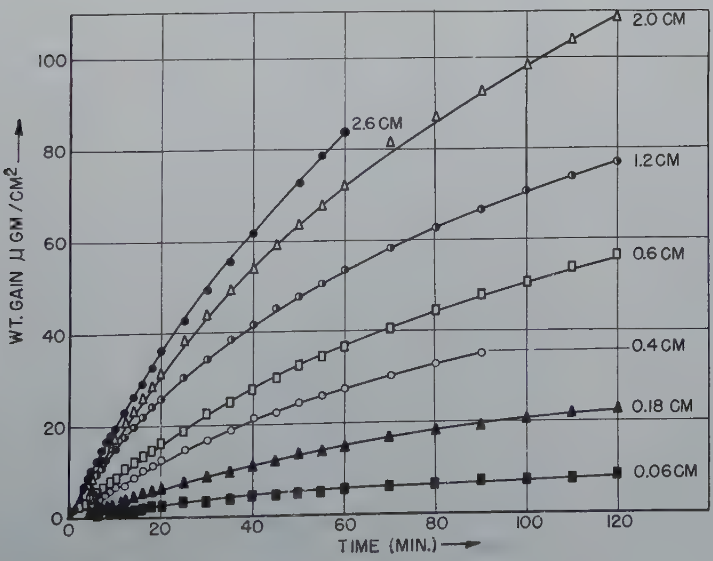

FIG 14—Reaction Zr with H_2 300°C. Effect of pressure.

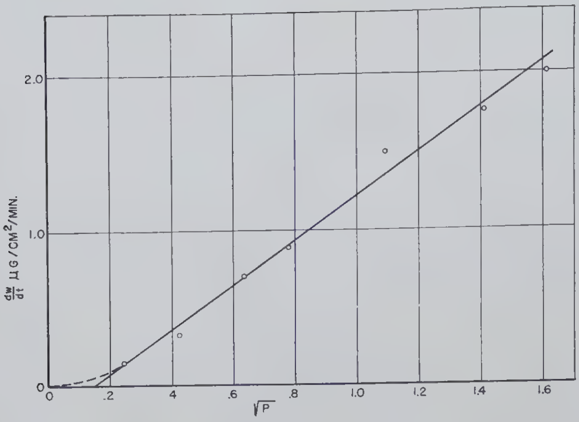

FIG 15—Reaction Zr with H_2 300°C. Initial reaction rate vs. $P^{1/2}$.

rate-pressure relationships have been found:

(1) Activated diffusion without dissociation $\frac{dW}{dt} = -kpe^{-b/T}$

(2) Activated diffusion with dissociation $\frac{dW}{dt} = -kp^{1/2}e^{-b/T}$

Here $\frac{dW}{dt}$ refers to the rate of reaction, p the pressure, t the time, T the temperature and k and b are constants. This expression predicts for the diffusion of atoms in the crystal of zirconium at constant temperature an expression of the type $\frac{dW}{dt} = Ap^{1/2}$.

It is rather surprising that the reaction does not follow one of the rate-pressure relationships. This evidence indicates that the reaction is not occurring on a bare metal surface but rather through a film of the nitride, the nitride in turn dissolving in the metal. Upon evacuation the nitride continues to dissolve but no further film formation is possible. After a certain time bare metal will be exposed and this is the condition in which we find the metal after completion of the experiment. The thickness of the nitride film is governed by the rate of reaction which is a reciprocal function of the thickness and the rate of solution of the nitride. The square root relationship of pressure is not expected to govern a reaction in which a film is present since the nitride is diffusing under a constant concentration gradient.

REACTION WITH HYDROGEN

The reaction is studied as a function of time, temperature and pressure. The stability of the reaction product is studied as a function of the temperature under high vacuum conditions. Fig 12–16 show the results. The hydrogen is prepared by diffusion through a palladium tube after a preliminary purification. A maximum pressure of 2.6 cm of hydrogen is used in the experiments since greater pressures required rather long preparation times.

Fig 12 shows a preliminary study of the reaction as a function of temperature for a pressure of 2.2 cm of hydrogen. The reaction appears to start at a temperature of 235°C and the rate of reaction increases rapidly with the temperature. A visual examination of the film showed no evidence of a surface film. It is assumed that the hydrogen is dissolving in the metal to form a compound or stable complex. On evacuating the hydrogen from the specimen shown in Fig 12 no decomposition is noticed. This evidence supports the point of view that the hydrogen is forming a compound or complex.

1. *Time and Temperature:* It is of interest to examine the time behavior of the reaction rate. Typical curves are shown in Fig 13 for temperatures of 250° to 300°C. The reaction rate falls off with time. An analysis of the change of slope with time shows that there is no great difference in the way the rate is changing with time for the three curves in spite of the great difference in the amount of hydrogen taken up during the reaction.

The 300°C curve after two hours of reaction shows a hydrogen uptake corresponding to the formula $ZrH_{0.216}$. Hall and co-workers[19] have found a saturation value of $ZrH_{1.95}$ for 20°C. No attempt is made to determine the saturation value.

If the rate determining process in the uptake of hydrogen is the diffusion of hydrogen into the metal, it is possible to account qualitatively for the decrease in reaction rate as due to a change in the diffusion constant D or to a change in the concentration gradient.

2. *Temperature:* A study of the reaction with hydrogen as a function of temperature is necessary if the details of the reaction mechanism are to be worked out. However, the reaction is very sensitive to the pretreatment and to the presence of surface films. In addition, the reaction is very sensitive to temperature, especially in the temperature range of 275° to 300°C. Very little reaction occurs at 250°C while at 300°C a very rapid reaction rate is observed. The temperature coefficient has not been determined for this reaction.

3. *Pressure:* The effect of pressure on the permeability of metals to hydrogen has been discussed by Barrer[1] and summarized in the section on *Reaction with Nitrogen* of this paper. Two possible rate-pressure relationships were proposed: (1) Activated diffusion without dissociation, and (2) activated diffusion with dissociation. Mechanism (2) is expected to govern the diffusion of hydrogen in metals since the openings in the metal structure are not large enough to allow molecules to diffuse directly.

The reaction rate may then be expressed at a constant temperature as follows:

$$\frac{dW}{dt} = Ap^{1/2}$$

Fig 14 shows the effect of pressure on the time course of the reaction for a temperature of 300°C. The pressure is varied from 2.6 to 0.06 cm. The results show that pressure has a large effect on the reaction.

To test the application of the square root law Fig 15 shows a plot of the initial reaction rate $\frac{dW}{dt}$ as a function of $p^{1/2}$. Good agreement is observed. This correlation shows that the diffusion of hydrogen into the metal is mainly by atoms of hydrogen.

It may be noticed that the curve bends at low pressure and is not linear with $p^{1/2}$ in this range. This effect has been discussed by Smithels and Ransley[29] for the permeation of hydrogen through metals. The rate should include a term which is a function of the fraction of surface covered θ.

4. *Stability:* Fig 16 shows the stability of the hydrogen complex with zir-

conium as a function of temperature in a vacuum of 10^{-6} mm of Hg. H_2 is added to zirconium at 250°C and 2.5 cm pressure. After evacuation the temperature is gradually raised. The temperature is given at the top of the graph. At a temperature of 436°C the hydrogen is given off. All of the hydrogen is removed as is shown in the figure. Above 700°C the specimen is reacting with its environment and gaining weight. We are not sure whether the specimen is readsorbing hydrogen and other gases given off by the furnace. The addition of hydrogen to a low pressure appears to increase this reaction.

Conclusion

The kinetics of the reactions of ductile zirconium with oxygen, nitrogen and hydrogen are studied as a function of time, temperature, pressure, surface preparation and stability of the particular film. The vacuum microbalance method is used for all of the measurements.

The oxidation reaction showed an appreciable rate at 200°C. No simple rate law is found to fit the data over a wide temperature range. However, the modification of the parabolic rate law suggested by Mott predicts the general shape of the time curve. An analysis of the parabolic rate law plots for long periods of reaction time shows straight lines. Using the transition state theory of gas-metal reactions an energy of activation of 18,200 cal per mol and an entropy of activation of −25.6 cal per mol per °C are calculated. These are compared to similar calculations on other metals.

A study of the temperature dependence of the oxidation rate as a function of film thickness shows a constant relationship. This fact suggests that one mechanism is controlling the rate over a wide thickness range. No evidence was found for an unstable oxide.

The nitride reaction is of special interest. The reaction is found to be very sensitive to traces of oxygen and hydrogen in the reacting gas. The rate of reaction of zirconium with nitrogen is much slower than the reactions with oxygen and hydrogen. The data agree well with the predictions of the parabolic rate law although reaction films are not observed on the metal. An energy of activation of 39,200 cal is calculated from the temperature coefficient of the parabolic rate law constants.

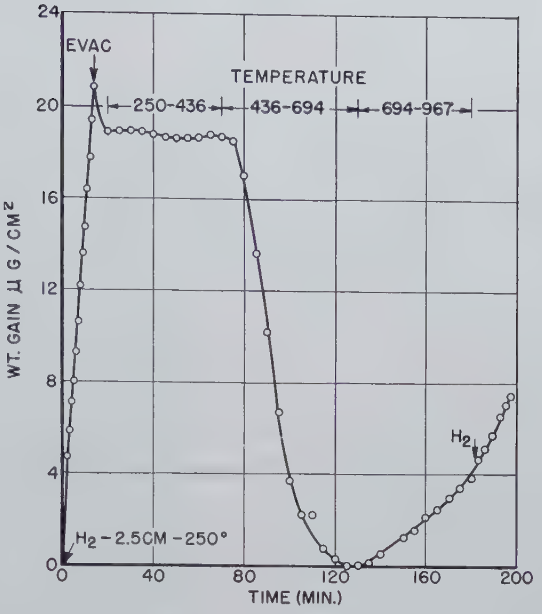

FIG 16—Stability of Zr hydride 250°–1000°C.

The nitride reaction is insensitive to pressure and the reaction does not follow any simple pressure function. A theory of the reaction is presented in which the limiting factor is the diffusion of the nitride into the metal under the conditions of a constant concentration at the surface.

The stability of the nitride is tested and the nitride is found to be stable to a temperature of at least 900°C.

The hydride reaction obeys the square root of pressure law. In this case, a film is not formed and it appears that hydrogen diffuses into the zirconium lattice as atoms. The time behavior of the reaction deviates from a linear law. This deviation may be due to changes in the concentration gradient in the metal or to a change in the diffusion constant. The hydride is stable in vacua up to a temperature of about 440°C

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Discontinuous Crack Propagation

L. D. JAFFE,* Junior Member, AIME, E. L. REED,* and H. C. MANN*

It has been generally believed that fracture originates at a point and, if the stress is sufficient, propagates across the material from this point. Evidence to the contrary is given in Fig 1. This micrograph shows an area close to the fracture of a steel containing

C	Mn	Si	Cr	Mo	V
0.28	0.74	0.20	1.00	0.49	0.12

The material had been quenched from 1675°F and tempered at 1150°F as a round about 10 in. in diam, and had a static tensile strength of 132,000 psi and a static yield strength of 105,000 psi. The steel was broken in 3000 cycles of reversed bending at a nominal max. fiber stress of 110,000 psi at a speed of 10,000 rpm. It was in the form of a standard R.R. Moore specimen with 45° V-notch, 0.015 in. radius and 0.220 in. diam at base of notch. The fractured edge in Fig 1 is part of the central portion of the specimen which broke during the final sudden fracture.

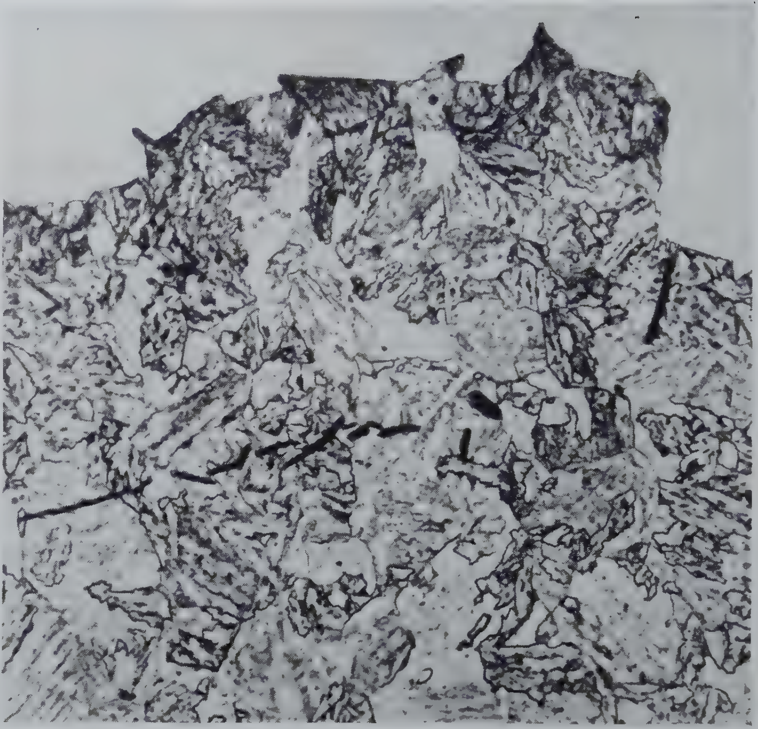

FIG 1—Microcracks near fracture of fatigue test specimen. × 500. Vilella etch.

Attention is directed to the short cracks which appear as dark lines within the specimen. Similar cracks were found in another specimen of the material, broken in 1,798,000 cycles at a nominal stress of 40,000 psi. The cracks were found in several areas close to the path of the final sudden fracture. This final fracture appeared microscopically to be wholly brittle and transcrystalline. Closer to the surface of the specimens, near the path of progressive fracture, which presumably advanced gradually during many cycles, there was microscopic evidence of some local deformation, but no microcracks. Neither were microcracks observed in areas distant from the main fracture path.

The following explanation is offered: In the sudden fracture of the specimen, a crack propagates along a crystallographic plane, with little or no plastic deformation of the adjacent material, until it reaches a grain boundary or a particle of carbide or inclusion which stops its advance. (The particle or boundary may be outside the plane of polish and not visible in the micrograph.) A stress concentration occurs about the end of the stopped crack. One or more new cracks are likely to start in the zone of this stress concentration. They may lie in the same grain as the first crack or in an adjacent grain. New cracks may occasionally start in a nearby but not adjacent grain whose orientation with respect to the stress leads to more ready fracture than does that of the grain between. Once started, these cracks propagate along crystallographic planes in their grains and the process repeats. This leads to discontinuous, branching chains of microcracks.

As the process continues, microcracks probably tend to link up by fracture of intermediate material under the influence of increasing stress concentration. Occasionally, too, there may be a series of nearby grains of similar orientation so that there is a certain continuity of fracture across them. In either case the effective size of a crack is increased, resulting in greater stress concentration at its ends and a greater likelihood of further increase of size of the continuously-fractured region. When one continuous crack crosses the entire specimen, macroscopic fracture has occurred. The fractured edge of the specimen in Fig 1 represents a series of microcracks which became continuous across the entire specimen. The short, dark-appearing cracks in the figure did not become continuous over a large area. The row of microscopic stress concentrations at their ends may link up with those of the "main crack" outside the plane of polish.

The above explanation does not imply that microcracks develop at the same rate in all portions of the specimen. They will develop most rapidly where the macroscopic tensile stress and macroscopic stress concentration are greatest. Viewed on a scale large compared to the grains, the fracture would appear to progress continuously across the specimen.

Although Fig 1 shows a specimen broken in a fatigue test, it is believed that the microcracks discussed do not depend on the repetitive nature of the stressing used, since they are in the region where "sudden" fracture occurred, presumably in a single stress cycle. The whole process of microcrack propagation outlined above is thought to have occurred during this single cycle.

It is believed that discontinuous crack propagation may be universal in brittle transgranular fracture of crystalline solids. Further experiments are under way.

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* Watertown Arsenal Laboratory, Watertown, Mass.

The Active Slip Systems in the Simple Axial Extension of Single Crystalline Alpha Brass*

ROBERT MADDIN,† Junior Member, C. H. MATHEWSON,‡ Member, and W. R. HIBBARD, Jr.,‡ Junior Member AIME

Recent publications[1,2] establishing the presence of cross-slip in strained metallic single crystals oriented wholly within the area of single slip as predicted from the generalizations of Taylor and Elam[3] described these markings as they appeared during the initial stages of the deformation process. At that time, the plane having a common glide direction with the primary slipping plane was reported as the cross-slip plane although the specific direction was not confirmed. Consequently, in continuation of the research, it seemed advisable to investigate the micrographic appearance of cross-slip together with the Laue back-reflection X ray analysis and stress-strain data during the later stages of the deformation process.

Accordingly, a single crystal of brass (72.75 pct Cu, 0.01 pct Fe, 0.01 pct Pb, 27.23 pct Zn) was polished mechanically and repolished electrolytically after the manner described in the earlier paper.[1] Three pairs of flat surfaces, parallel to the specimen axis, and (1) perpendicular to the plane containing the pole of the primary glide plane and the specimen axis, (2) perpendicular to the plane containing the pole of the cross-slip plane and the specimen axis, and (3) perpendicular to the plane containing the slip direction and the specimen axis, were polished mechanically and repolished electrolytically, resulting in a final minimum gauge diameter of 0.4864 in. in a gauge length of 3.36 in. The specimen was elongated in tension and load-extension readings were taken following the method described in the initial investigation.[1] Observed reorientations were obtained from a series of Laue back-reflection photograms at the center and ends of the gauge length and at various positions around the circumference of the specimen. These were interpreted after the manner of A. B. Greninger.[4]

Micrographic Observations

Cross-slip (Fig 1 and 2) was found with the first appearance of the primary slip clusters and usually joined members of these clusters. In addition, a third set of entirely different markings (Fig 3) could be noted. The displacement of this third set by the primary slip lines was measured as 8300 at. diam (3.04 microns). Since the specimen was carefully observed at high magnifications before any deformation and no markings of any type could be noted, it would appear that this third set was formed during the deformation process prior to the initiation of classical primary slip.

Additional extensions produced no unusual change in the appearance of either cross-slip or the third set of markings. The number of lines increased with increasing elongation and appeared, generally, in areas where earlier markings were present. The continuity of the clusters of cross-slip lines in Fig 4, 5 and 6 illustrates that they are neither noticeably displaced by nor do they displace the primary lines at this stage. In Fig 7, cross-slip appears in a long narrow localized band approximately 45 degrees from the stress axis. This somewhat resembles a twin band except for the lack of a sharp boundary.

After a shear of 0.257, sufficient additional glide occurred on the cross-slip plane to displace the primary slip lines (Fig 8). Generally, where a large number of cross-slip lines could be observed in an area on one flat surface, few cross-slip lines appeared on the diametrically opposite position on the parallel flat (Fig 9). These, of course, were not matched observations on the same glide ellipses. It was extremely difficult to make such comparisons.

The third set of markings (Fig 10) was extensively displaced by glide on the primary slip planes. A plot of the width of primary slip clusters versus their displacement of the third set of lines is shown in Fig 11. The slope and the linearity of the plot suggest that each primary glide plane slips to a constant maximum value of shear before further slip is transferred to another plane. A shear value of 0.28 was determined in this case. Heidenreich[5] has presented a similar schematic representation of glide for aluminum.

After the specimen had attained an elongation of 51.8 pct, corresponding to a shear of 0.973, cross-slip appeared very prominently in certain areas as shown in Fig 12, yet at diametrically opposite positions very little cross-slip could be noted, Fig 13. Classical conjugate slip was found at this advanced stage in the deformation, Fig 14, which corresponds to the axial location shown at 12 in Fig 15. It should be noted that cross-slip occurs within the conjugate slip clusters and on the same plane as the cross-slip associated with the closely spaced primary lines which constitute a background in less distinct focus.

The third set of markings noted at all stages in the deformation of the

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† Research Fellow in Metallurgy, Yale University, New Haven, Connecticut. Recently appointed Assistant Professor of Mechanical Engineering, The Johns Hopkins University, Baltimore, Maryland.
‡ Professor of Metallurgy and Assistant Professor of Metallurgy, respectively, Yale University.

[1] References are at the end of the paper.

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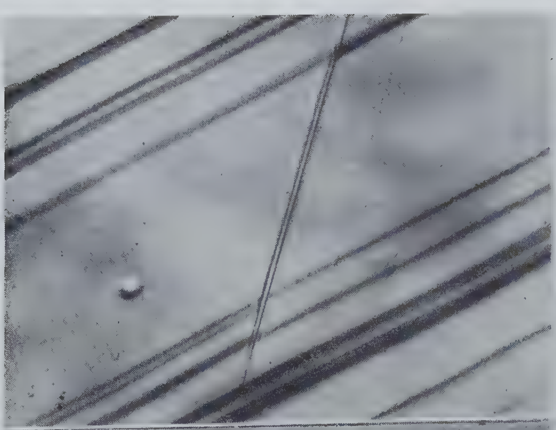

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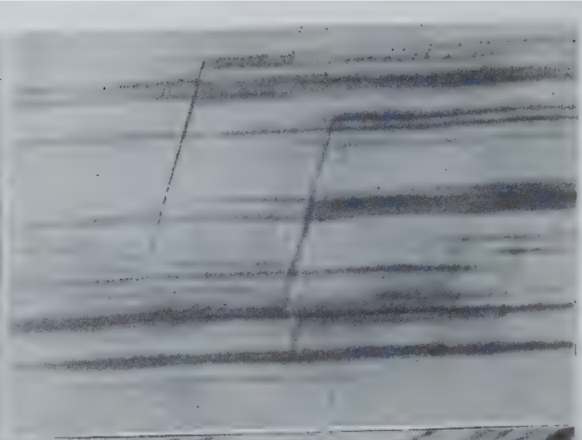

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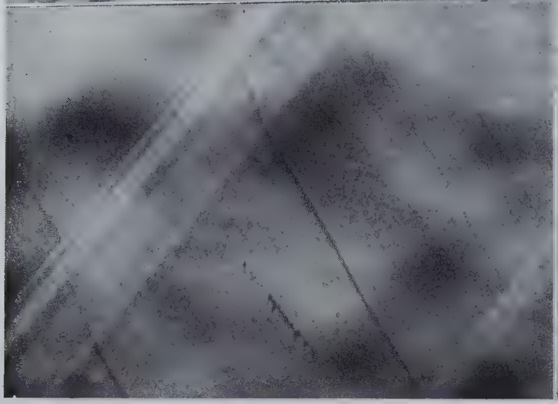

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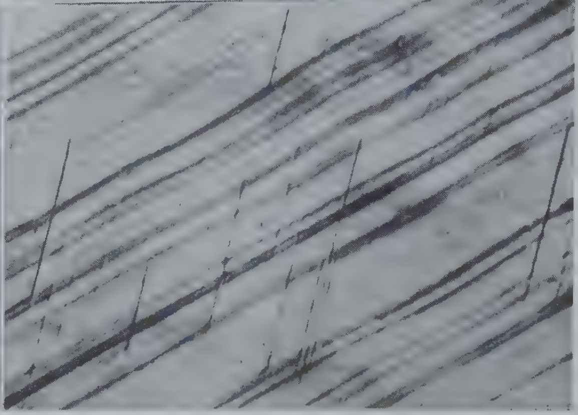


FIG 1—Resolution of cross-slip lines at a position perpendicular to the plane containing the slip direction and the specimen axis. Stress axis is vertical.
Shear is 0.0009. × 1000

FIG 2—Prominent cross-slip at a position perpendicular to the plane containing the pole of the primary glide plane and the specimen axis. Stress axis is vertical.
Shear is 0.053. × 1000

FIG 3—Displacement of a third set of markings by a cluster of primary slip lines at a position perpendicular to the plane containing the pole of the cross-slip plane and the specimen axis. Stress axis is vertical.
(Oblique illumination) Shear is 0.0009. × 1000

FIG 4—Relatively long segmented cross-slip lines at a position perpendicular to the plane containing the slip direction and the specimen axis. Stress axis is vertical.
Shear is 0.102. × 1000

specimen was found in perfect alignment with the classical conjugate slip lines and hence it may be concluded that both effects were caused by the same family of octahedral planes.

In order to observe critically the direction of slip on the cross-slip plane, a crystal was prepared as in the previous manner but without any flat surfaces. It was then extended an amount sufficient to produce a large number of slip lines.

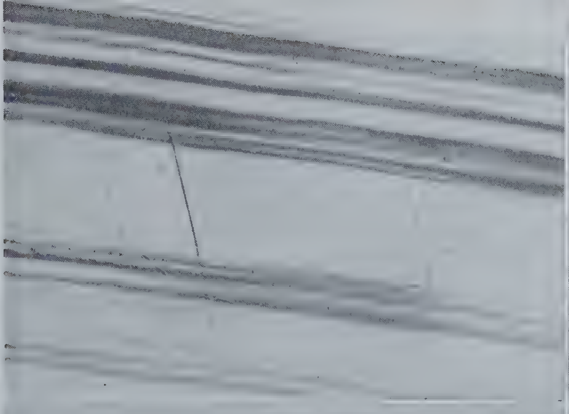
In any metallic single crystal, slip lines are visible because the linear translation of the glide planes displaces the surface. There are, however, two positions (180 degrees apart) on the circumference of a cylindrical crystal at which this displacement is parallel to a surface plane and hence slip lines would not be visible. These positions lie in planes containing the specimen axis and the slip direction.

By observing the presence or absence of cross-slip in planes parallel to the plane containing the specimen axis and each of the three possible slip directions in turn, the plane of observation in which cross-slip could no longer be observed would identify the direction of slip. The technique becomes critical if the three observation planes are suitably placed about the periphery of the cylindrical specimen. Accordingly, careful microscopic observations were made at all positions on the circumference of the crystal. The position where cross-slip could not be observed coincided with the position where primary slip lines could no longer be seen. Furthermore, since cross-slip could be seen at all other positions, two of the three possible slip directions were eliminated. Hence it may be concluded that both the primary and cross-slip planes possess the same slip direction.

Summarizing this situation, the slip systems involved in the plastic extension of the face-centered cubic alpha brass are: 1. The (primary) system required by the classical Taylor and Elam analysis. 2. A system exhibiting the octahedral plane which contains the same slip direction as the first octahedral plane, now constituting the active direction as in the other system. 3. The conjugate system required by the classical Taylor and Elam analysis. 4. A system exhibiting the octahedral plane which contains the same slip direction as the plane normally acting in conjugate slip, now constituting the active direction as in the case of the conjugate system.

The slip produced by System 2 was originally termed "cross-slip" because its trace as observed in the first experiments cut across the trace of the primary slip and the early evidence of other cross markings now traceable to the conjugate slip system (acting prematurely) was not conclusive.

It should be noted that the same "cross-slip" plane is associated with both primary slip and conjugate slip but the direction differs in accordance with the associated plane. Therefore, three slip planes and two directions



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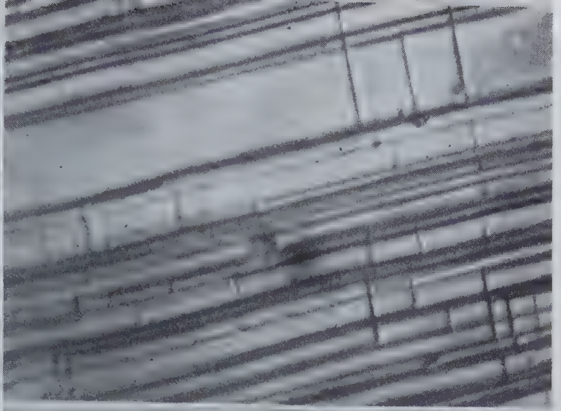

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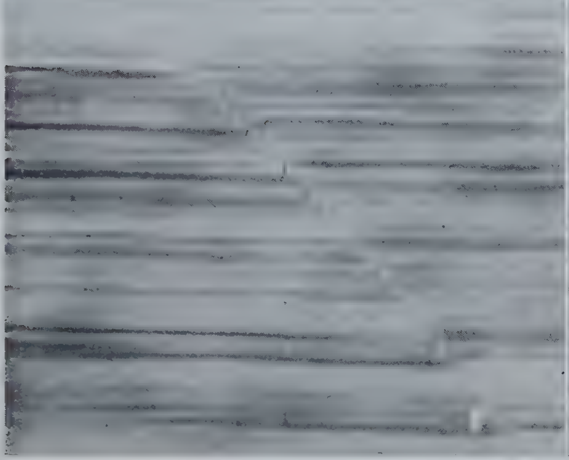

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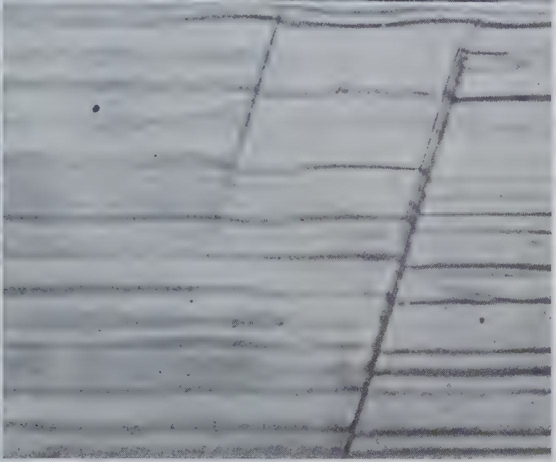

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FIG 5—Appearance of primary and cross-slip lines perpendicular to the plane containing the specimen axis and the slip direction. Stress axis is vertical.
Shear is 0.102. × 1000

FIG 6—Clustered cross-slip at a position perpendicular to the plane containing the slip direction and the specimen axis. Stress axis is vertical.
Shear is 0.174. × 1000

FIG 7—"Twin" appearance of cross-slip at a position perpendicular to the plane containing the pole of the primary glide plane and the specimen axis. Stress axis is vertical.
Shear is 0.174. × 1000

FIG 8—Displacement by cross-slip lines of the primary slip lines at a position perpendicular to the plane containing the pole of the primary glide plane and the specimen axis. Stress axis is vertical.
Shear is 0.257. × 1000

of slip have been observed in these experiments.

X-ray Results

No measurable amount of asterism could be noted in the Laue spots during the deformation corresponding to shears through 0.463. At the beginning of classical conjugate slipping, a large amount of asterism could be observed. In some cases, the streaks encompassed as much as seven degrees.

After the crystal had been elongated 12.8 pct corresponding to a shear of 0.257, Debye rings amounting to at least 20 degrees of arc could be seen in the back-reflection photograms corresponding to areas such as those shown in Fig 8, whereas they could not be observed in photograms representing areas of the type shown in Fig 9. This effect became more pronounced throughout the specimen during the later stages of the deformational process. At the beginning of classical conjugate slip, the fragmentation rings, sometimes as great as 180 degrees of arc, could be noted wherever there was a dense concentration of cross-slip (Fig 12) but was noticeably absent for areas of the type shown in Fig 13.

The lattice rotations for the various extensions of the specimen are plotted in Fig 15. These rotations follow, generally, the theoretically predicted course. It may be noted, however, that in the initial stages of deformation, the reorientations observed from the X ray data exceeded the calculated; they agreed in the vicinity of the symmetry curve and, in the final stages, the observed reorientations lagged behind the theoretical.

It may be well to point out that for the first five extensions, λ and χ values (λ is the angle between the specimen axis and the slip direction, and χ is the angle between the specimen axis and the primary slip plane) were observed from a series of photograms made only at the center of the specimen, whereas, the λ and χ values for the last seven extensions were averaged from photograms made at the ends and center.

Stress-strain Results

The initial stress-strain curve for the specimen with a constant rate of loading of 100 lb per min. is plotted in Fig 16. Correspondingly, stress-strain curves for several series of consecutive loadings of the crystal to the yield point, generally with the same rate of loading, are plotted in Fig 17, 18, 19 (a larger shear and a ten-fold increase in the rate of loading) and 20. It may be noted that no noticeable rise in proportional limit results from this type of extension. However, by plotting the first loading of each group superimposed upon one another, Fig 21 is obtained, in which it is evident that strain hardening

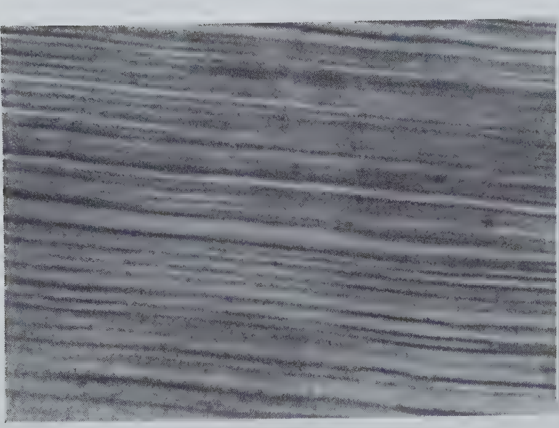

FIG 9—Lack of cross-slip and density of primary slip lines on a surface diametrically opposite to the one shown in Fig 8. Stress axis is vertical.
Shear is 0.257. × 1000

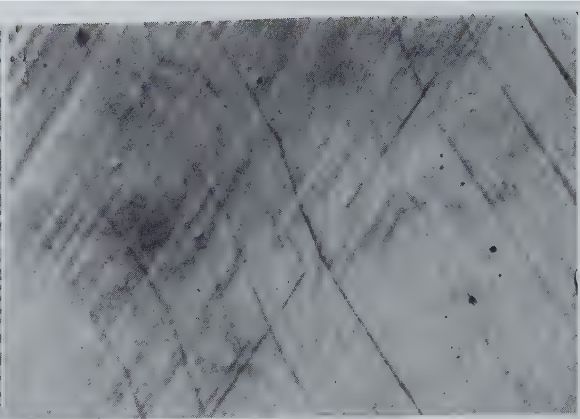

FIG 10—Displacement of the third set of markings by primary slip lines about 30 degrees from a position perpendicular to the plane containing the slip direction and the specimen axis. Stress axis is vertical.
Shear is 0.257. × 1000

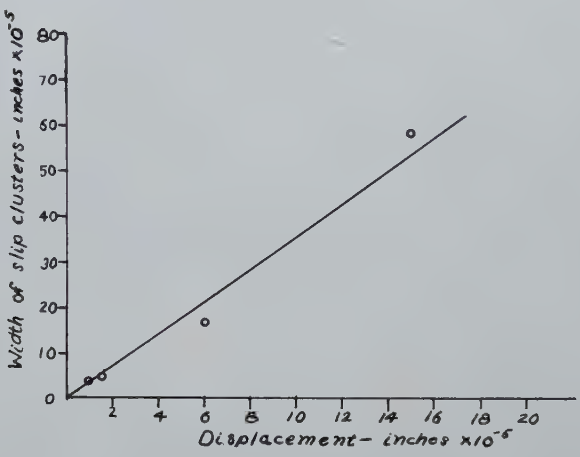

FIG 11—Displacement of the third set of markings by primary slip clusters of different widths.
Data obtained from Fig 10.

has occurred. Moreover, the plot of the critical resolved shear stress for each of these curves against the prior shear, Fig 22, is in good agreement with the strain hardening curve for brass of the same composition as reported by von Göler and Sachs.[6] Whereas the von Göler and Sachs curve, Fig 23, indicates that shear strengthening begins at a value of shear of about 0.18, the present curve shows that hardening begins at a value located between shears of 0.174 and 0.257. Beyond these points there is apparently a sharper rise in the present curve than in the one reported by von Göler and Sachs.

Discussion of Results

The methods by which the different parts of a metallic single crystal reorient during deformation and at the same time adjust themselves to the constraints of adjacent matrix material and the specimen grip ends have been the subject of many investigations. These investigations have postulated in the main a bend-gliding mechanism (*Biegegleitung*)[7] and a crystal fragmentation[8] followed by the rotation of minute crystallites. Asterism has been cited as evidence of both these mechanisms. However, the absence of asterism and the presence of collateral slip on hitherto unpredicted systems in a strained crystal oriented wholly within the hypothetical single slip region suggest that the above postulated mechanisms can be considerably modified, perhaps in the direction of simplification.

Consider, for example, the constraints imposed by the material adjacent to a latent glide plane. Once slip has occurred along this plane forming a visible slip line at the surface, the crystal has already reoriented. The actual reorientation can be considered as formative during the gliding and completed once the slip line has appeared. Consequently, in order for reorientation to occur, the gliding plane must be in a state of flexure (of the type reported by Polanyi[7]), caused by the stresses due to the unslipped adjacent material. This bending causes compression of the gliding plane on the concave side and tension on the convex side and is assumed to be directed about an axis in the plane of slip at right angles to the direction of slip (<112>). A set of octahedral planes favorably situated to reduce these stresses would be the conjugate slip planes which cut across the primary planes at a wide angle (70 degrees) and it is not surprising to observe their participation in the process long before the advent of classical conjugate slip. Bending moments arising from the action of these intersecting octahedral planes would be opposite in the rotational sense although not entirely symmetrical since the <112> axes in question do not lie in the same plane. In order to produce glide plane curvature without plastic action, the potential glide plane would have to be bent elastically in the modified sense of elastic shear and flexure outside the range of perfect elastic behavior, that is, by an anelastic process or an initial elastic stage of flexural gliding. However, instead of full flexural glide, relief could take place by action of the conjugate slip planes just prior to slip on the primary glide plane carrying the highest conventionally resolved shear stress. It might be predicted, therefore, not only that a set of secondary markings would always be associated with the primary slip lines but that this set would also be displaced by the primary lines. This was found to be the case with the present specimens in which the markings in question have been described as the third set, and with other

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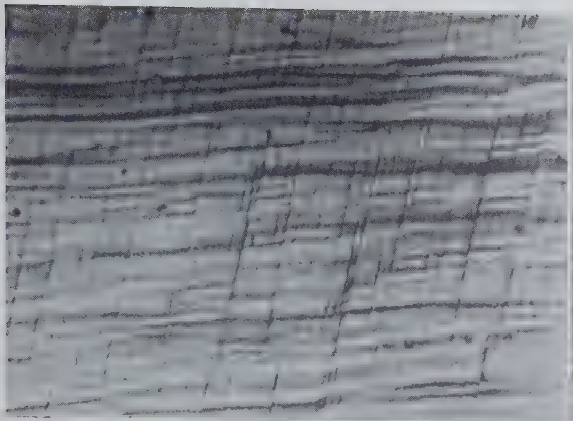

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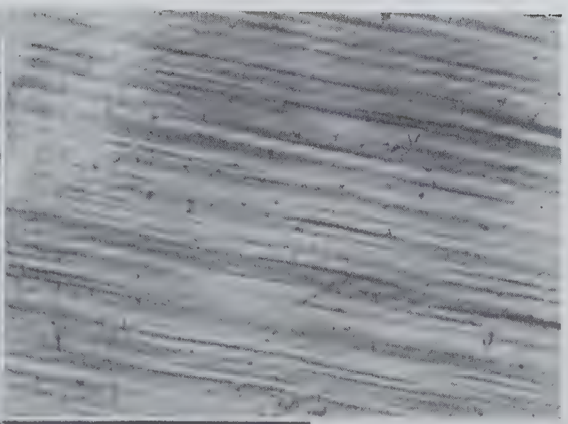

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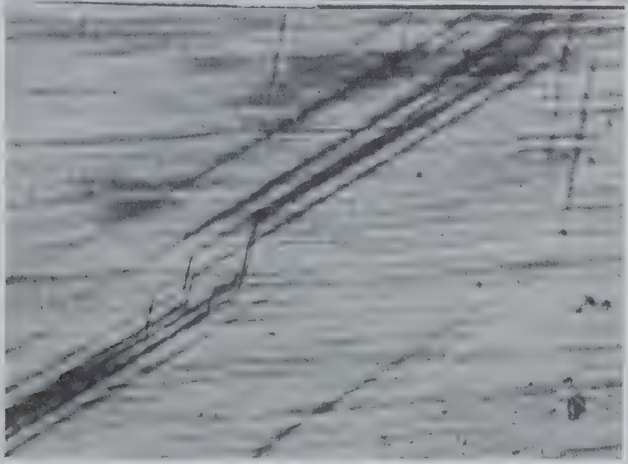

FIG 12—Dense cross-slip at a position perpendicular to the plane containing the pole of the primary glide plane and the specimen axis. Stress axis is vertical.
Shear is 0.973. × 1000

FIG 13—Absence of cross-slip at a position diametrically opposite the one shown in Fig 12. Stress axis is vertical.
Shear is 0.973. × 1000

FIG 14—Conjugate slip cluster showing cross-slip in both the conjugate slip cluster and the primary slip lines at a position perpendicular to the plane containing the pole of the primary glide plane and the specimen axis. Stress axis is vertical.
Shear is 0.973. × 1000

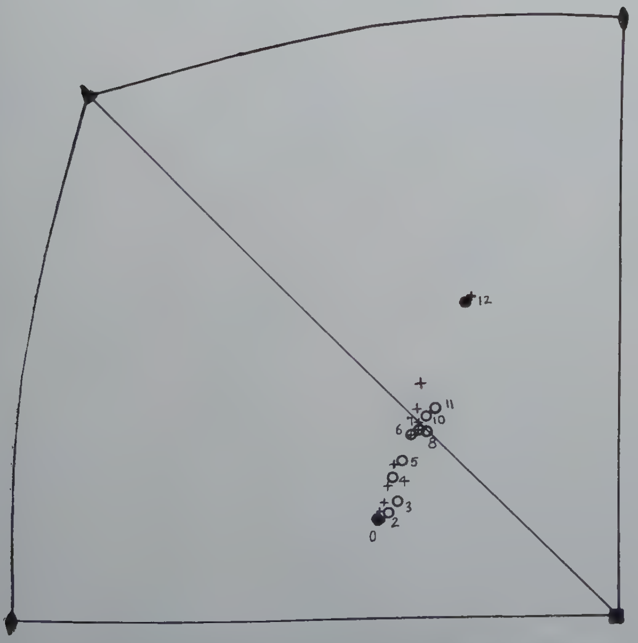

FIG 15—Theoretical and observed lattice rotations for crystal investigated. Numbers refer to specific loading.
+ Theoretical position after successive loading
o Observed positions

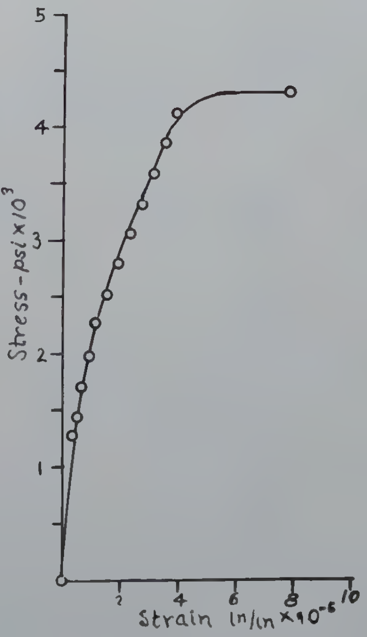

FIG 16—Initial stress-strain curve.

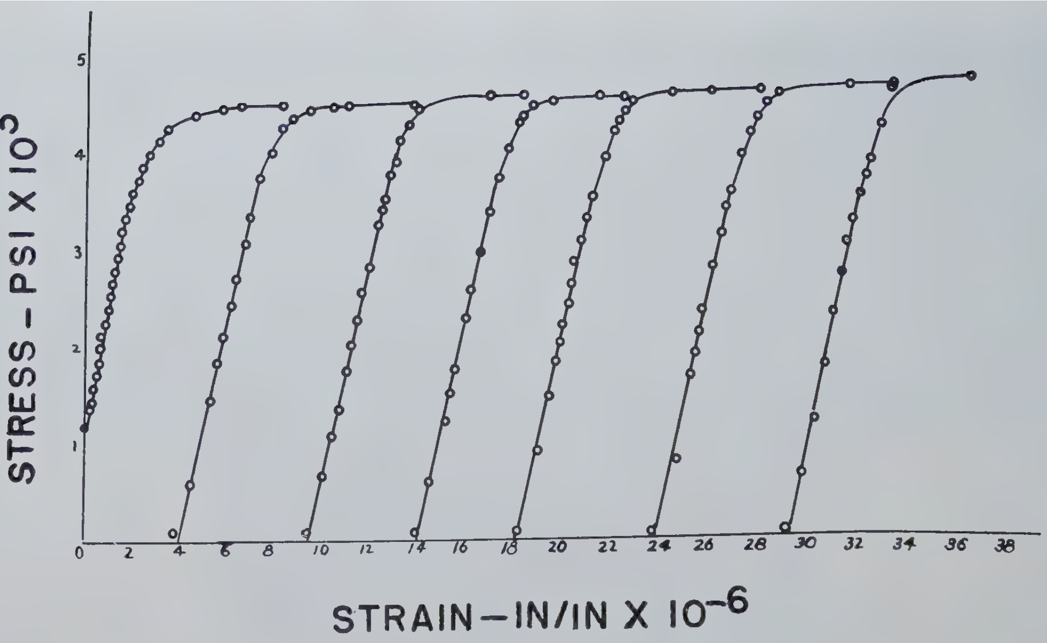

FIG 17—Seven consecutive loadings of the specimen to its yield point.
Prior shear is 0.174.

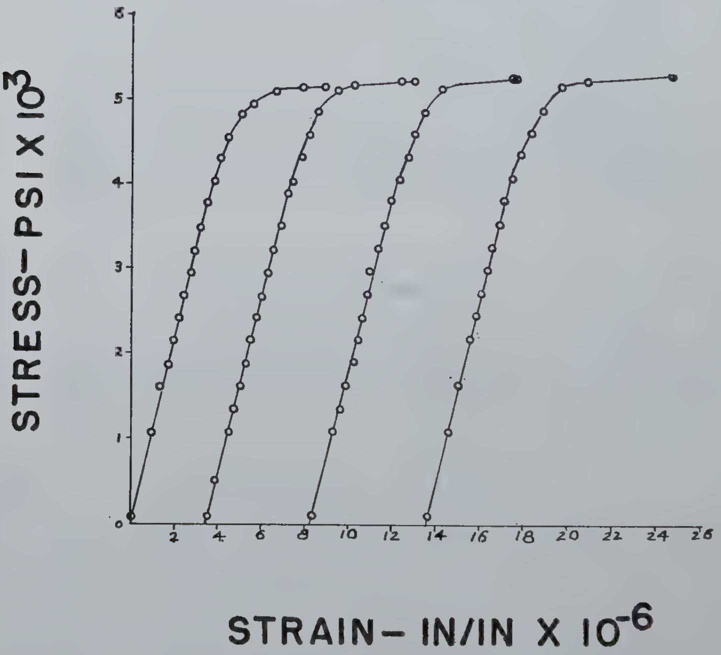

FIG 18—Four consecutive loadings of the specimen to its yield point.
Prior shear is 0.257.

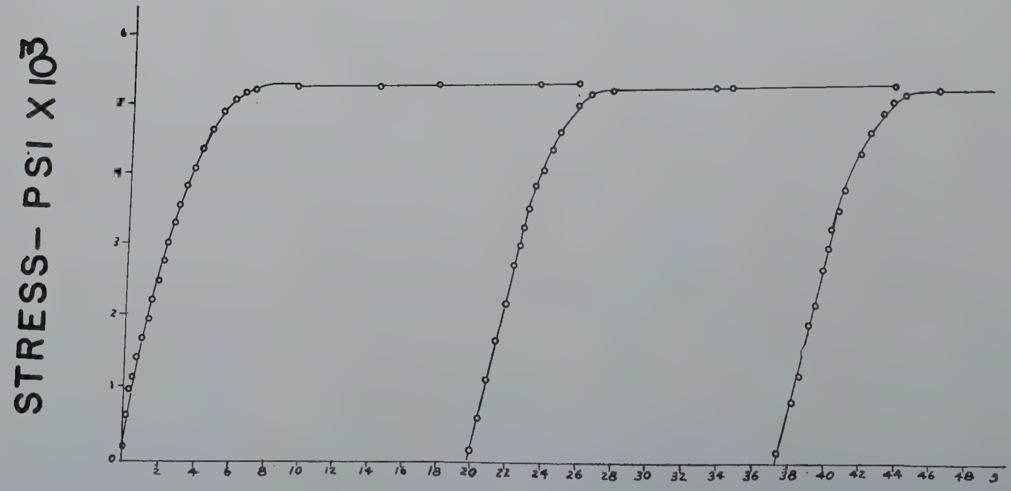

FIG 19 (left half)—Six consecutive loadings of the specimen to its yield point. Rate of loading is 1000 lb per min.
Prior shear is 0.265.

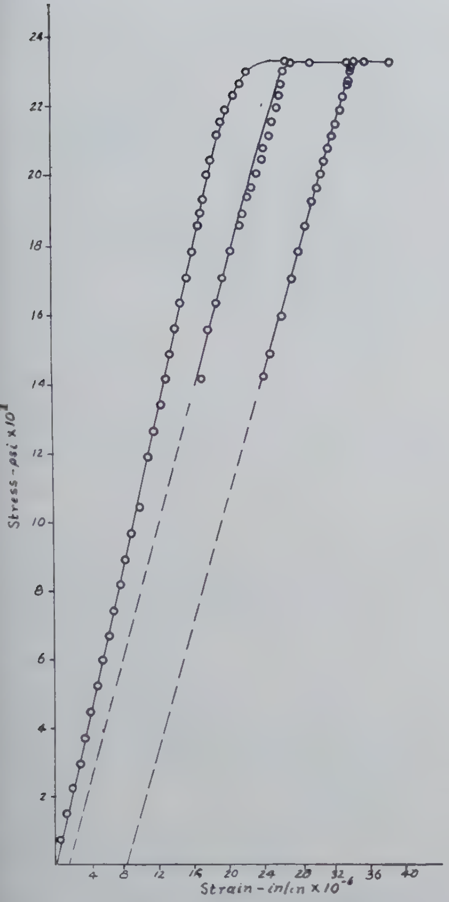

FIG 20—Three consecutive loadings of specimen to its yield point.
Prior shear is 0.973.

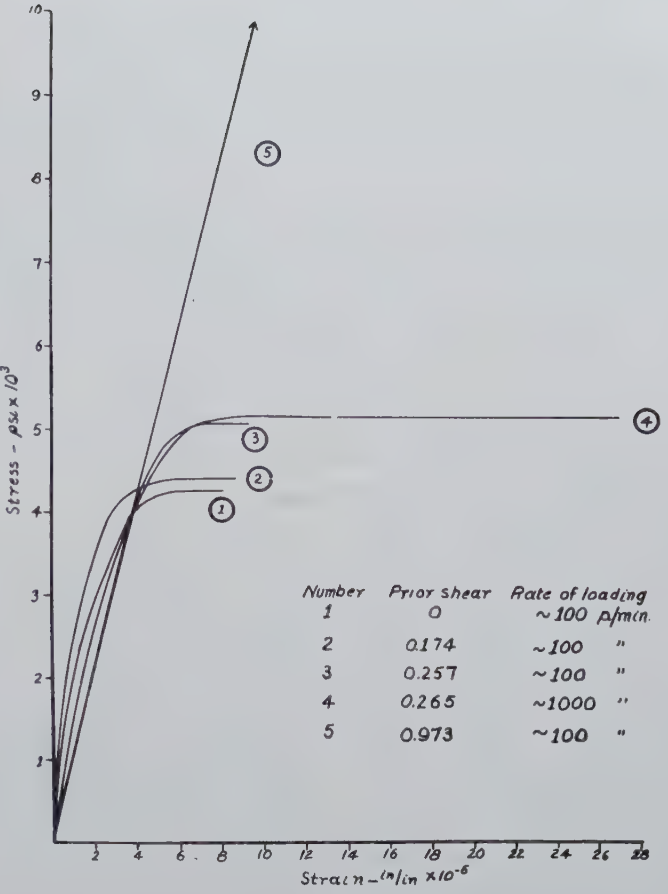

FIG 21—Superimposed stress-strain curves for the first loading of each total extension shown in Fig 16, 17, 18, 19 and 20.

crystals investigated in the Hammond Laboratory.

The cross-slip plane was identified as the one having a common slip direction with the major slip plane. Since it has also been found that the slip direction is the same for both the cross-slip plane and the major slip plane, shear may now be pictured as occurring simultaneously along a pair of planes forming steplike folds, with the cross-slip plane corresponding to the short leg of the fold. Whether this can be clarified in the mechanics of stress action in a perfect crystal with regard for inhomogeneities at the stepped ends of the lamellae, or must be explained in terms of dislocations or other abnormalities in the crystal must be determined by further study.

In the initial stages of the deformation process, back-reflection Laue photograms were made with the X ray beam incident in the central region of the crystalline rod where the major deformation had occurred as shown by the much larger number of slip lines in this area. Consequently, the lattice reorientation observed from the X ray data exceeded the reorientation as calculated from the initial and final gauge lengths representing the over-all elongation of the specimen. In the vicinity of the symmetry curve where the theoretical and observed reorientations agreed, slip had taken place throughout the crystal and the X ray data represented an average of exposures made at different points of

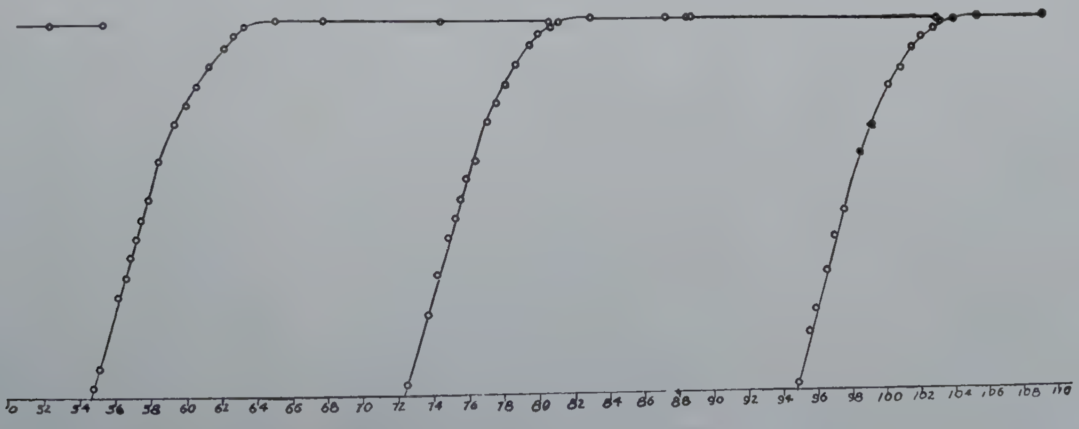

FIG 19 (right half)—Strain—in/in × 10⁻⁶.

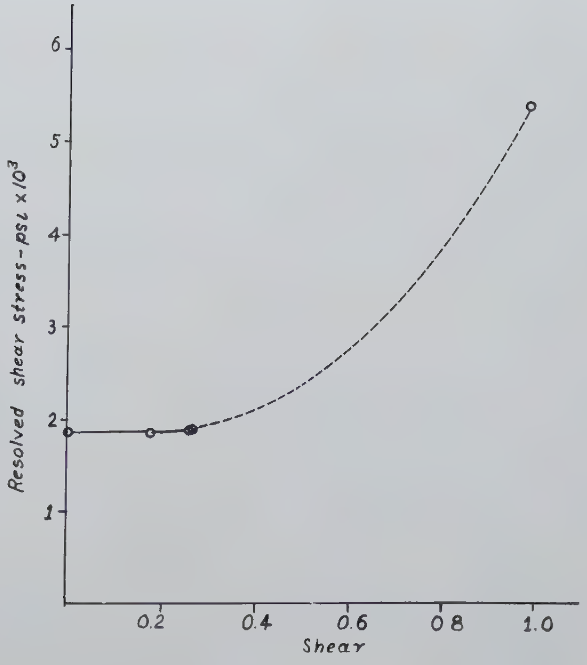

FIG 22—Shear strengthening curve for specimen investigated.

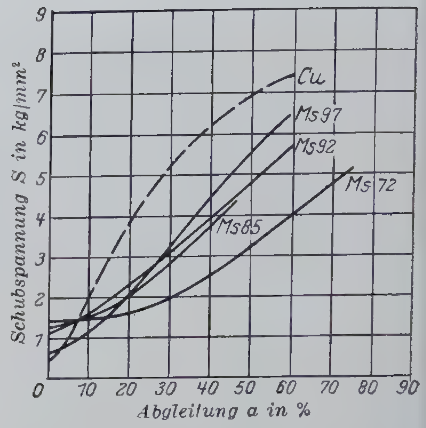

FIG 23—Shear strengthening curves for copper and a series of brasses.
(von Göler and Sachs)

the specimen and thus gave a more truly representative macro-history of the lattice reorientation.

In the later stages, the observed reorientations lagged behind the theoretical ones. This lag has previously been reported by von Göler and Sachs.[6] An explanation of this latter behavior might stem from a consideration of the additional amount of glide on the cross-slip planes as compared with the small amount during the early stages of deformation. Cross-slip first occurred either simultaneously or in close association with primary slip since neither the primary nor the cross-slip lines were displaced. During the later stages of deformation, however, additional glide occurred on the cross-slip planes as noted by their displacement of primary lines. In this way, the theoretical reorientation did not represent the true reorientation since it gave no account of glide on the cross-slip planes.

Although consecutive loadings to the yield point show no strain hardening, shear strengthening can be observed after the separate extensions. One possible explanation for this behavior might be sought in the hypothesis that recovery rates are greater while deformation is proceeding than after deformation has stopped.

Summary

The observations reported seem to suggest that plastic deformation in single crystals of alpha brass of approximately 70-30 composition begins by gliding on octahedral planes possessing cross-slip folds. This stage of the deformation process is not accompanied by measurable strain hardening. To cause slip to proceed along planes segmented into folds would conceivably require a greater stress than along other planes and, consequently, slip is diverted to undisturbed areas. Hence there would be no over-all measurable strain-hardening. When all available unslipped areas are eliminated, it would seem that greater stress would be required to cause further glide in previously slipped areas. This stage of the deformation process appears to be the beginning of shear strengthening and would be accompanied by the occurrence of further glide on the cross-slip and primary slip planes. Since shear strengthening begins to occur at about the point where additional glide has also occurred on the cross-slip planes as well as on the primary planes and since this stage of the deformation process is accompanied by notable fragmentation wherever there is a large amount of prominent cross-slip it would seem that shear strengthening may be caused primarily by the necessity of forcing glide along planes segmented into folds. With additional deformation which increases fragmentation, the stress rises sharply until the classical stage of conjugate slip begins. Cross-slip also occurs during conjugate slip and on the same slip plane that operated before true conjugate slip began. When associated with either the primary or conjugate slip plane it assumed the appropriate common direction.

Acknowledgment

The authors' thanks are due to the Bridgeport Brass Company for having supplied the brass rod from which the crystals were made.

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The Effects of Molybdenum and Commercial Ranges of Phosphorus upon the Toughness of 0.40 Pct Carbon Chromium Steels

M. BAEYERTZ,* Member AIME, W. F. CRAIG, JR.* and J. P. SHEEHAN*

This paper deals with molybdenum modifications of 5140 steel that have the same hardenability but a better tolerance for phosphorus than the AISI-SAE 5140 grade. Lack of toughness in steels with higher than normal phosphorus contents is well known to metallurgists. This problem is troublesome even within normal phosphorus ranges, if the heat treatment or the design of the part or the service is critical. Under such unfavorable conditions and also in the case of phosphorus contents toward the upper side of the commercial range, the use of molybdenum to replace a part of the chromium in 5140 steel provides a factor of safety.

The toughness of steel is variously exhibited in different mechanical tests; broadly the term is applied to the capacity of the steel to deform prior to fracture. Defined in this way, toughness is considered to be an inherent quality that depends upon the composition and structure of the steel, and also upon its temperature during deformation and fracture in the test. In the present state of our knowledge, the type of mechanical test needs to be included in any discussion of toughness, because the revelation of this quality in steel depends on the stress state and rate of stressing imposed by the test.

In comparing the toughness of one steel with another by laboratory testing, it has long been customary to use notched tests that impose severe constraint to deformation, and then to test over a range of temperatures to obtain the so-called transition. At temperatures above the transition, the steel fails after considerable deformation and absorption of energy. Below the transition, less energy is absorbed as the steel fails largely by cleavage. The transition range itself is characterized by a more or less abrupt change in energy absorption and type of fracture. The conventional V-notch Charpy impact test has been used exclusively in the work covered by this report. For the steels under study, rather sharp transitions are obtained with this test, at testing temperatures that are easily obtained in the laboratory. The position of the transition on the testing temperature scale provides a rather sensitive index of the toughness of the steel, when the steels under study are similar in character as they are in this work.

Turning to the metallurgical reasons for the greater toughness of one steel as compared to another, the authors propose to limit the discussion to the small field under study. Only one structural state is considered, tempered martensite of a hardness of about 28 Rockwell C or 269 Brinell. The study deals first with the loss of toughness in AISI-SAE 5140 steel caused by increasing the phosphorus content from about 0.020 to 0.040 pct. A second part of the work deals with counteracting this loss in toughness by replacing a part of the chromium by molybdenum. A series of molybdenum modifications was studied, in each of which the chromium was reduced sufficiently to duplicate the hardenability of 5140 steel.

Phosphorus affects the toughness of steel in two ways. An inherent lack of toughness of phosphorus-bearing ferrite as compared to low phosphorus ferrite has often been noted. Jolivet and Vidal[1] have shown that phosphorus has the same effect in tempered martensite in chromium steels. The other well known effect of phosphorus is to make steel susceptible to temper embrittlement. Temper brittleness is a loss in toughness brought about by tempering steel within a limited temperature interval somewhat below the A_1 temperature. In most of the standard AISI-SAE alloy steels, this temperature interval is approximately 850–1100°F. Either of these types of loss in toughness is easily followed by the shift in the transition temperature obtained with the notched-bar impact test. The data to be presented show the beneficial effect of substituting molybdenum for a part of the chromium in 5140 steel with either moderate (0.020 pct) or high (0.040 pct) phosphorus contents. Both the inherent lack of toughness of phosphorus-bearing steel and temper brittleness are counteracted by this use of molybdenum.

The work of Jolivet and Vidal mentioned above shows the detrimental effect of phosphorus on the toughness of tempered martensite in the absence of temper embrittlement, as well as the temper brittleness caused by phosphorus. They used two steels, essentially 0.25 pct C-1.4 pct Cr, with 0.044 and 0.012 pct P, respectively. The nonembrittled state was obtained by quenching in oil from 1610°F, then tempering for one hour at 1200°F and quenching in water. In this state the transition temperature range of the low phosphorus steel in the notched-bar impact test was below that of the steel with 0.044 pct P. An additional treatment of 24 hr at 975°F (that is, in the embrittling range) caused both steels to lose toughness, but the high phosphorus steel showed the greater embrittlement.

Recently Hollomon[2] has published a comprehensive survey and bibliography of the literature on temper brittleness, to which the reader is re-

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TP 2654 E. Disussion of this paper (2 copies) may be sent to *Transactions* AIME before December 1, 1949. Manuscript received June 22, 1948; revision received May 2, 1949.

* Armour Research Foundation of Illinois Institute of Technology.

[1] References are at the end of the paper.

ferred for a general review of the subject. Carbon, nitrogen, phosphorus, oxygen, and various alloying elements as well have been blamed for the embrittlement. Other pertinent papers have appeared subsequently. Cohen, Hurlich, and Jacobsen[3] and McLean and Northcott[4] have studied metallographic etchants for revealing the temper brittle state. Pellini and Queneau[5] have obtained data which they interpret as indicating carbon to be the cause of temper brittleness. Their conclusion is based on the observation of isothermal development of brittleness at temperatures below the A_1 temperature but above that of the iron-nitrogen eutectoid. In the light of data to be presented later in this paper, it may be noted that their steel that developed brittleness at this high temperature contained 0.029 pct P, an amount which might be suspected as the cause of the embrittlement.

The inception of the case against phosphorus, as a factor in temper brittleness, dates from World War I. However, in this early work and to some extent in later investigations conclusions are based on tests made only at room temperature. Andrew[6] reported that steels with phosphorus in the lower part of a range of 0.01 to 0.058 pct did not exhibit temper brittleness, while in the upper part of this phosphorus range the difference in impact strength between water quenched and slowly cooled specimens was as much as 50 pct.

Ashdown[7] stated that temper brittleness was observed in large chromium-nickel steel forgings with phosphorus contents of 0.03 to 0.04 pct while he also observed its absence in aircraft crankshaft forgings of the same steel except with phosphorus below 0.02 pct.

Data presented by Andrew[6] and also by Green[8] show the influence of phosphorus in a series of 0.35 pct C-3.5 pct Ni steels alike in composition and treatment but with variable phosphorus content. The 0.018 and 0.039 pct P steels had susceptibility ratios of one; in those with 0.058 pct and higher phosphorus contents the ratio rose consistently with the phosphorus content. The susceptibility ratio is the impact value of the unembrittled steel divided by that of the same steel in the embrittled state. The ratio applies to a single testing temperature, usually room temperature.

Greaves and Jones[9] obtained similar data using Cr, Ni and Cr-Ni steels with about 0.3 pct C, from which they concluded that phosphorus up to 0.04 pct has little influence on temper embrittlement but that higher phosphorus has a marked effect in raising the susceptibility ratio.

Reporting work on various plain carbon and alloy steels, Mauer, Wilms and Kiessler[10] and also Bischof and Bottger[11] have added to the observations of the deleterious effect of phosphorus.

Bennek[12] studied the role of phosphorus in temper brittleness using susceptibility ratios, and in some instances supplemented these with determinations of the impact transition curves. Phosphorus contents ranged from less than 0.01 to 0.11 pct. Manganese, Ni, Cr, Cr-Ni and Cr-Ni-Mo steels were employed. Carbon contents were between 0.25 and 0.30 pct. Prolonged heating either above or below the critical range lessened the intensity of embrittlement developed on subsequent heat treatment; presumably phosphorus diffused from regions of high phosphorus segregation during the anneal. The low phosphorus steels exhibited little or no temper brittleness provided that the alloy content was restricted to 1.5 pct Mn, Ni, or Cr; however, a steel with 3.58 pct Ni, 0.92 pct Cr and only 0.012 pct P showed a marked shift in transition temperature on furnace cooling compared to water quenching after tempering. This apparent influence of hardenability on susceptibility to temper brittleness seems of importance, although, for fully hardened specimens, a reason is not obvious.

The greater tendency to embrittlement in steels containing both chromium and nickel, as compared to either alone, had often been observed by investigators of temper brittleness. Recently Hollomon[2] has shown a rather consistent relationship between the susceptibility ratio (specimens broken at −40°F) and the combined hardenability contributed by manganese, nickel, and chromium in a series of twenty-one 0.30 pct C, Cr-Ni-Mo steels. Manganese varied from 0.76 to 1.52 pct, nickel from a trace to 3.41 pct and chromium from 0.45 to 2.57 pct. Phosphorus was hardly variable as the entire range for the series was 0.009 to 0.014 pct.

Plan of Investigation

In the present work, a straight chromium grade was chosen to avoid the confusion of a number of alloying elements. Heats of 5140 steel were made with phosphorus contents varying between 0.020 and 0.036 pct. The lower side of the phosphorus range was selected in an attempt to duplicate a usual residual for open hearth steels. The upper side was chosen to fall within the AISI-SAE specification for the grade. Then, because molybdenum has been the element most widely used for reducing or delaying the onset of temper brittleness, another series of modified 5140 steels was studied in which a part of the chromium was replaced by molybdenum, keeping the hardenability essentially constant. Phosphorus was varied as in the 5140 series.

It might be argued that reduction in chromium content would assist in reducing the susceptibility to temper brittleness but, in adding molybdenum, either the hardenability of the steel or the basic 5140 composition must be altered. In view of the apparent relation between hardenability and temper brittleness noted by many investigators and also from the standpoint of providing a steel with the same hardenability as 5140 but with a good tolerance for phosphorus, the substitution of molybdenum for part of the chromium seemed the best procedure, and the one of greatest commercial significance. If molybdenum were added to the 5140 base analysis without reduction in chromium, the 4140 grade of considerably higher hardenability would be approached.

In both the 5140 steels and the molybdenum modifications aluminum was used to produce fine grained steels, which would be comparable with a large part of the commercial production of 5140. Another reason for adding aluminum was to remove both oxygen and nitrogen from the metal phase and thus materially reduce the possibility of a contribution to temper brittleness by these elements.

The tempering treatments were illustrative of common commercial cycles. In considering the choice of a tempering cycle, it is desirable to have reference specimens in an unembrittled state of the same hardness as the embrittled specimens. In isothermal studies this has been done by tempering all specimens between the A_1 temperature and the embrittling range and then quenching in oil or water. Subsequent isothermal treatment in the embrittling range does not change the hardness materially, and the quenched specimens without subsequent isothermal treatment provide a nonembrittled norm.

While isothermal tempering of small

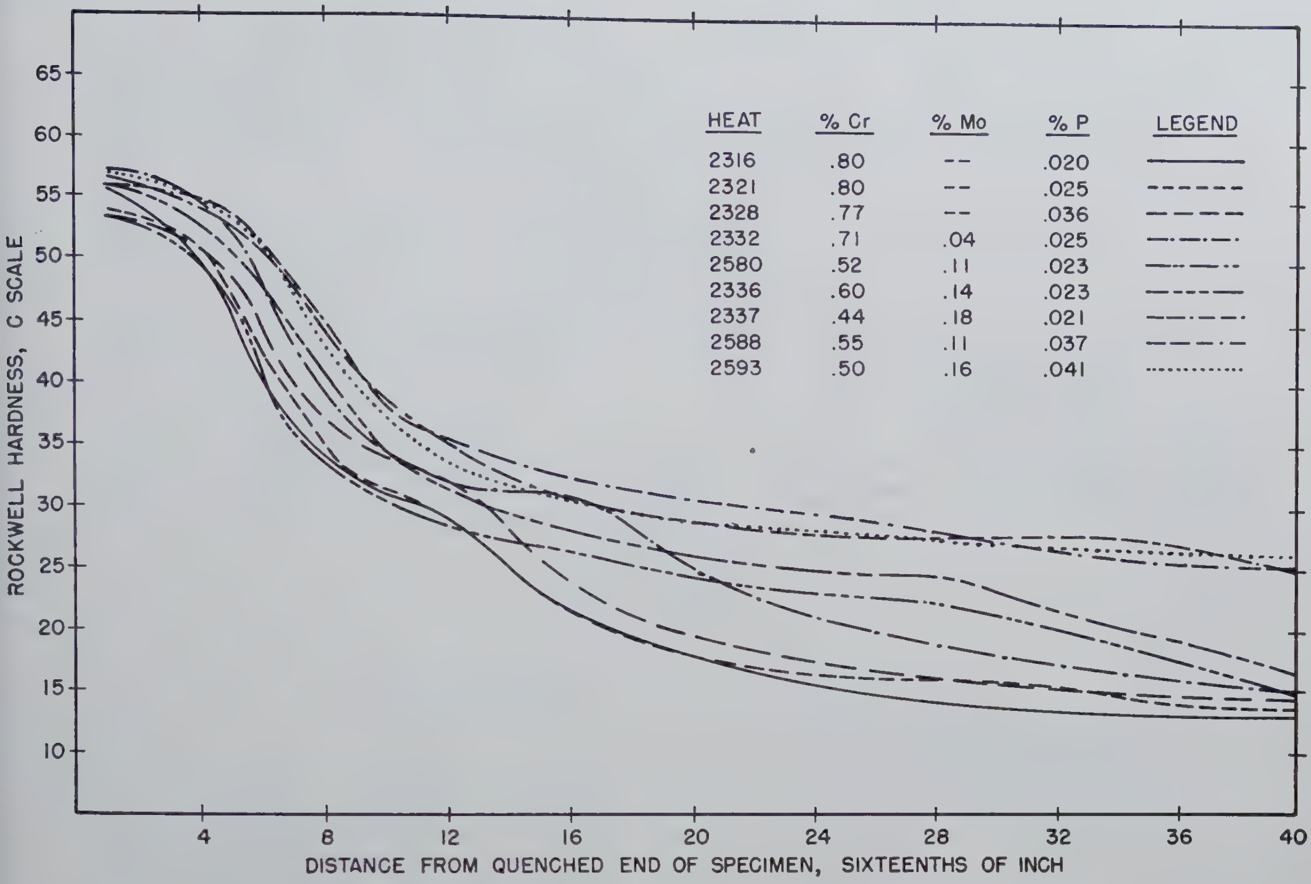

FIG 1—Hardenability band of 5140 and molybdenum-chromium steels with variable phosphorus.
Standard Jominy test, quenching temperature 1550°F.

specimens is attractive for the study of the embrittling reaction, it does not simulate commercial practice in the tempering of machine parts in which loss of toughness would be of practical importance. For the purpose of this work it seemed preferable to temper above the embrittling range and to obtain progressive embrittlement by cooling at various rates through the temper brittle range. A tempering temperature of 1150°F and a range of cooling rates wide enough to simulate those generally encountered in commercial heat treatment were chosen. Specimens quenched in water from the tempering temperature provided a nonembrittled norm for the evaluation of temper brittleness, and also for determination of the effect of the replacement of chromium by molybdenum on toughness in the nonembrittled state.

Another consideration in selecting the tempering treatment was the variable amounts of chromium and molybdenum in the steels, and the influence of these elements on the tempering rate. Their effect on tempered hardness is least at high tempering temperatures such as 1150°F chosen for this study. That the tempering treatments selected were fairly successful in obtaining uniform hardness is shown by a maximum range in Rockwell C values of 25 to 31 for both the 5140 and the molybdenum-chromium steels. The molybdenum-chromium steels tended to be slightly higher in hardness than the 5140 steels at each cooling rate, and the hardness of both series decreased slightly with slower rates of cooling from the tempering temperature.

The transition range of the notched-bar test was used as a measure of toughness.

Preparation of the Steels

In order to have comparable steels, 500 lb laboratory induction furnace heats were made, using Armco iron from a single open hearth heat as the charge. Uniform furnace practice was maintained. The steel was deoxidized with 1½ lb of aluminum per ton in the furnace. The analyses of the steels are given in Table 1.

As phosphorus is one of the elements most apt to segregate in steel ingots, it was desired that the experimental data would approach those which might be obtained with the same phosphorus contents in commercially produced steels. With this in mind, one ingot of 460 lb weight with hot top was poured from each heat and only the top half of each ingot was used in the study of temper brittleness.

The top halves of the ingots were forged to ½ by 2½ in. bars for the impact tests and 1¼ in. round bars for the Jominy tests. All stock was normalized from 1550°F and stress relieved at 1200°F prior to machining the specimens.

Determination of Hardenability

The standard Jominy test was used for the determination of hardenability. The Jominy bars were quenched from 1550°F. The hardenability band for the 5140 steels with variable phosphorus and for the molybdenum modifications is shown in Fig 1. The 5140 steels vary little in hardenability, but the band is unavoidably somewhat wider at the lower hardness levels as a result of the effect of molybdenum.

The austenite grain sizes of the various steels were ASTM No. 8 to 9, as determined by polishing a section from each Jominy test bar.

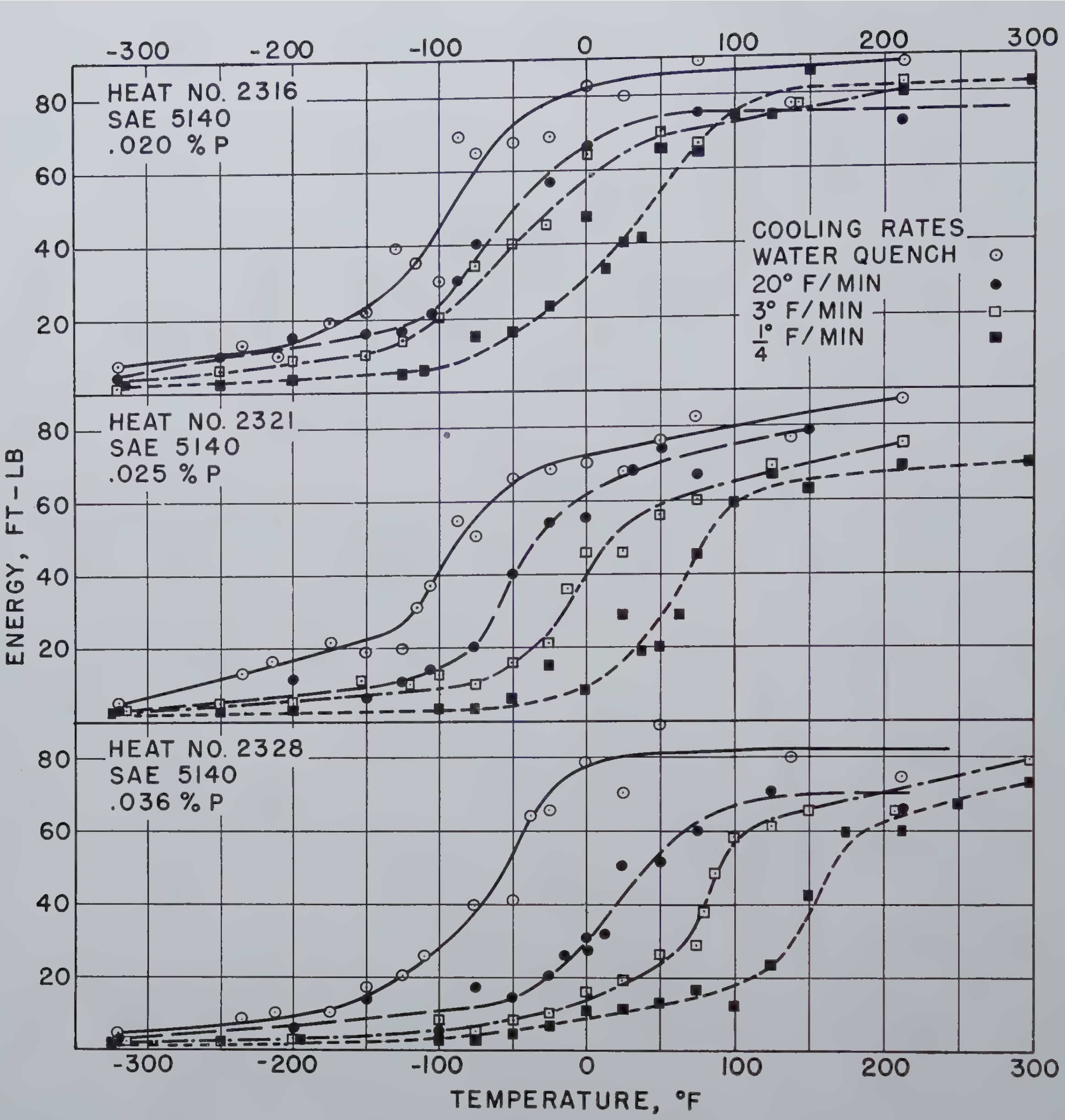

FIG 2—Impact transition curves for 5140 steel with variable phosphorus.
Specimens quenched in oil from 1550°F, tempered for one hour at 1150°F and cooled at the rates indicated in the legend.

Table 1 . . . Chemical Analyses

Grade	Heat	C	Mn	P	S	Si	Cr	Mo
5140	2316	0.44	0.73	0.020	0.025	0.26	0.80	
	2321	0.39	0.77	0.025	N.D.*	0.30	0.80	
	2328	0.42	0.76	0.036	N.D.*	0.27	0.77	
Mo-Cr	2332	0.43	0.72	0.025	0.027	0.26	0.71	0.04
	2580	0.41	0.81	0.023	0.020	0.24	0.52	0.11
	2336	0.43	0.73	0.023	0.024	0.20	0.60	0.14
	2337	0.40	0.79	0.021	0.021	0.26	0.44	0.18
Mo-Cr	2588	0.42	0.81	0.037	0.021	0.23	0.55	0.11
	2593	0.42	0.80	0.041	0.019	0.24	0.50	0.16

*Not Determined.

Determination of the Transition Ranges

Longitudinal Charpy specimens with a 45° V-notch of 0.010 in. root radius[13] were used. They were machined in groups of four from the central portion of the ½ × 2½ in. bars.

The specimens, 0.016 in. oversize, were heat treated before grinding to size and notching. The base of the notch was perpendicular to the longitudinal direction of the bars, and extended between the specimen surfaces representing the top and bottom, 2½ in. wide surfaces of the bars. The notches were roughed out with a high speed steel milling cutter, and finished with a carefully ground and checked carbide tipped fly cutter. The radii of the notches were 0.010 in. and were held to a tolerance of ±0.001 in. by checking every sixth specimen at 50 diam with an optical comparator.

The heat treatment consisted of quenching in oil from 1550°F, tempering for one hour at 1150°F and cooling at different rates from this temperature to 700°F. The cooling rates used were approximately ¼, 3, and 20°F per min., and water quenching. The 3 and 20°F per min. rates were nominal averages of the actual rates between 1150 and 700°F. The ¼°F per min. rate was maintained with a program controller. All specimens were cooled in air from 700°F.

Specimens of each steel with each treatment were broken over a sufficient range of temperature to determine the transition range. A Sonntag Universal impact testing machine of 120 ft-lb capacity and a striking velocity of 17 ft per sec was used. The capacity was raised to 240 ft-lb when impact values over 90 ft-lb were expected. The data

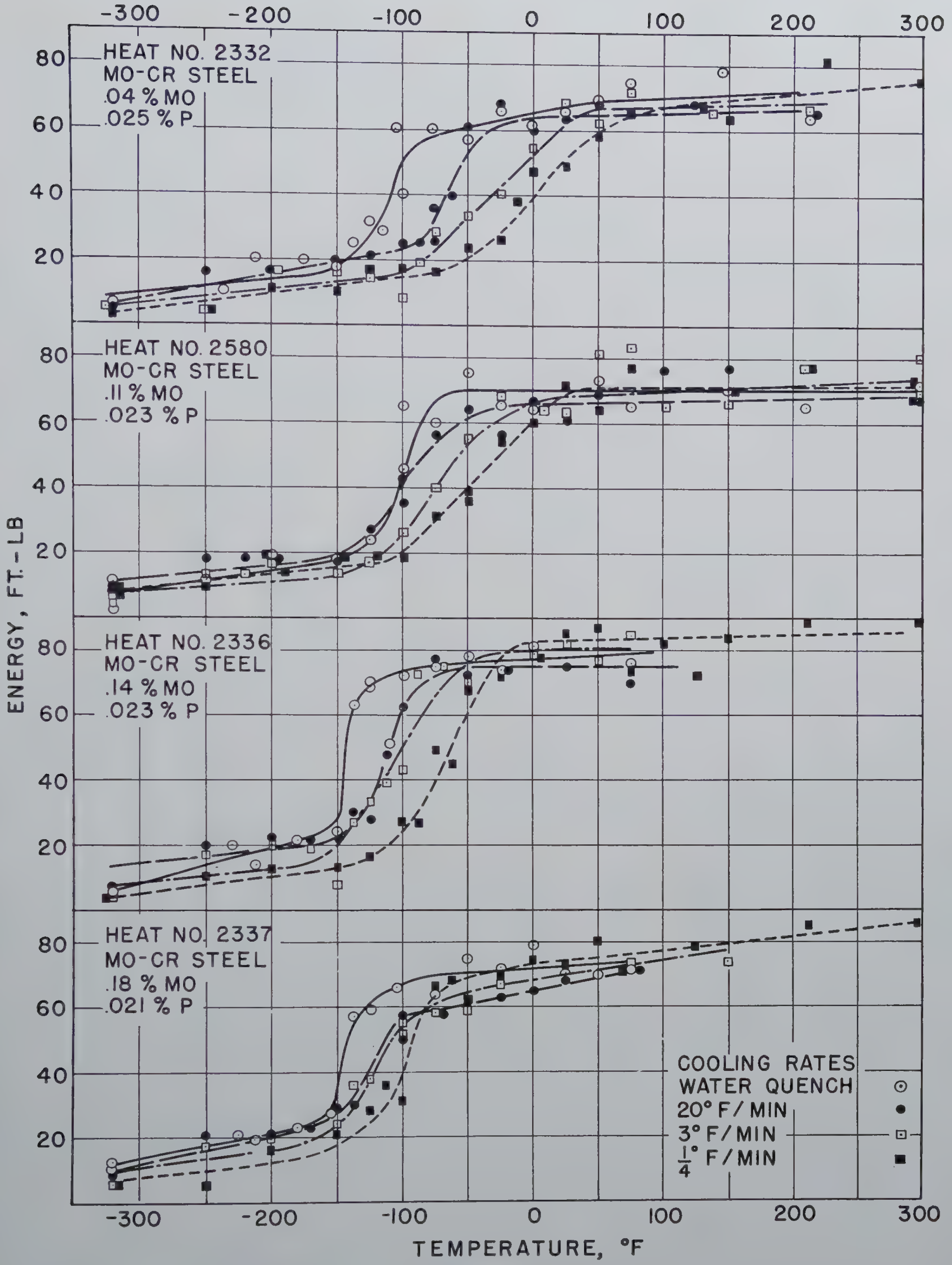

FIG 3—Impact transition curves for molybdenum-chromium steels with 0.021 to 0.025 pct phosphorus.
Specimens quenched in oil from 1550°F, tempered for one hour at 1150°F and cooled at the rates indicated in the legend.

are assembled in Fig 2, 3, and 4, in which the impact values have been plotted against testing temperatures in the conventional way. The points shown in the figures signify individual impact values, not averages. All of the data represent completely fractured specimens.

Rockwell C hardness values obtained on the impact specimens of the various steels with each cooling rate are listed in Table 2.

Effect of Phosphorus in 5140 Steel

Fig 2 illustrates the changes in toughness that attended an increase in phosphorus from 0.020 to 0.036 pct in 5140 steel. Even in the specimens that were quenched in water after tempering, a rise in the transition temperature range with increase in phosphorus content is to be noted. This agrees with the previously noted observations of Jolivet and Vidal. As it seems unlikely that quenching in water allows sufficient time for embrittlement during cooling of an impact specimen, this effect of

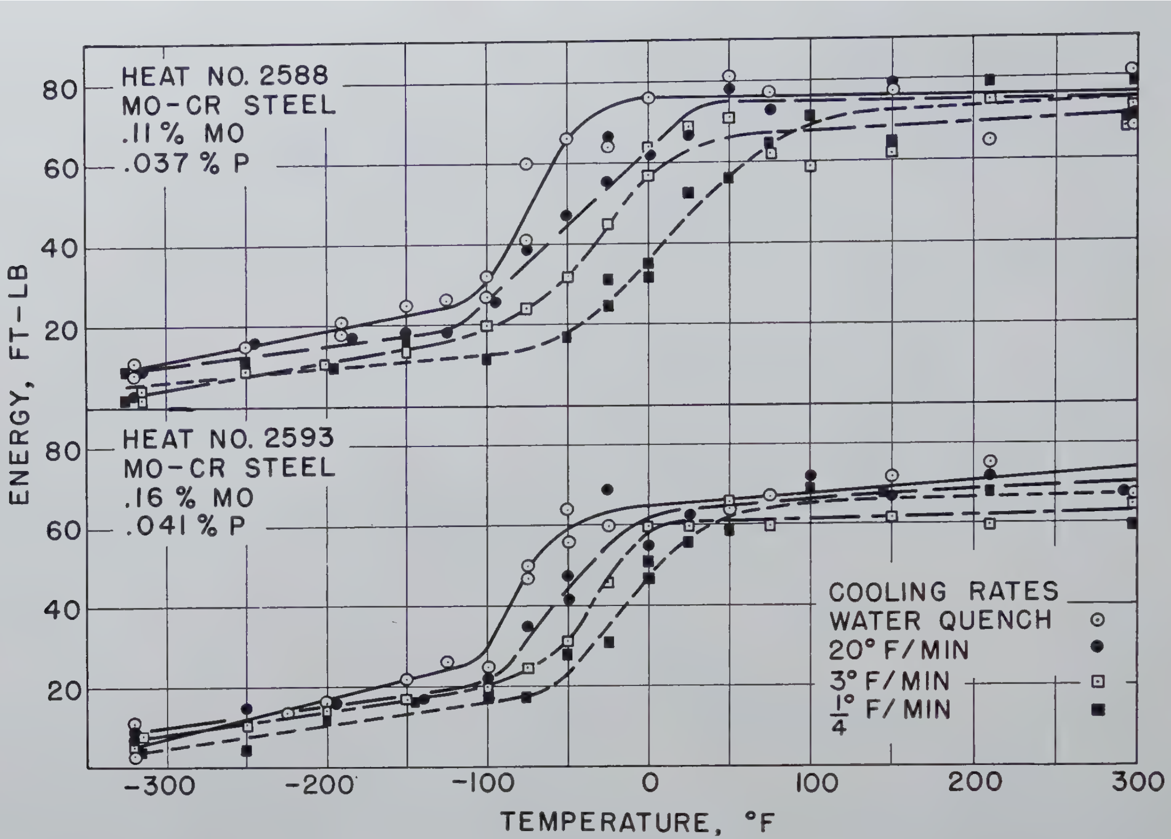

FIG 4—Impact transition curves for molybdenum-chromium steels with 0.037 to 0.041 pct phosphorus.
Specimens quenched in oil from 1550°F, tempered for one hour at 1150°F and cooled at the rates indicated in the legend.

phosphorus might be attributed either to inherent brittleness of the phosphorus-bearing ferrite phase in tempered martensite or to embrittlement during the period of tempering at 1150°F. While this question was not answered unequivocally, enough work was done to show that the result is essentially the same in tempering periods of one and three hours at 1150°F. Specimens from the three 5140 steels were heat treated in the same way as the water quenched specimens of Fig 2 except that the tempering period was extended to three hours. The impact transition curves for both the one- and three-hour treatments are shown in Fig 5. Only slight differences in transition were produced in each steel by the additional two hours at 1150°F. These data strongly suggest that the increase of phosphorus from 0.020 to 0.036 pct has raised the transition of 5140 steel, even in the probable absence of temper brittleness.

Table 2 . . . Average Rockwell C Hardness of Impact Specimens

Grade	Heat	Cr	Mo	P	Rockwell C Hardness, with Cooling Rate of:			
					Water Quench	20°F per Min.	3°F per Min.	¼°F per Min.
5140	2316	0.80		0.020	29	29	26	26
	2321	0.80		0.025	29	28	27	25
	2328	0.77		0.036	28	27	27	26
Mo-Cr	2332	0.71	0.04	0.025	31	30	29	28
	2580	0.52	0.11	0.023	28.5	28.5	27.5	26
	2336	0.60	0.14	0.023	30	28	27	26
	2337	0.44	0.18	0.021	31	30	30	27
Mo-Cr	2588	0.55	0.11	0.037	29.5	29.5	28.5	26.5
	2593	0.50	0.16	0.041	31	31	29.5	27

Table 3 . . . Transition Temperatures Read from Fig 2, 3, and 4 at Impact Value of 45 Ft-Lb

Grade	Heat	Cr	Mo	P	Transition Temperature, °F, with Cooling Rate of:			
					Water Quench	20°F per Min.	3°F per Min.	¼°F er Min.
5140	2316	0.80		0.020	−100	−55	−35	35
	2321	0.80		0.025	−95	−40	10	75
	2328	0.77		0.036	−60	30	85	160
Mo-Cr	2332	0.71	0.04	0.025	−105	−60	−20	10
	2580	0.52	0.11	0.023	−100	−95	−65	−40
	2336	0.60	0.14	0.023	−145	−115	−105	−70
	2337	0.44	0.18	0.021	−145	−120	−115	−95
Mo-Cr	2588	0.55	0.11	0.037	−80	−50	−25	20
	2593	0.50	0.16	0.041	−80	−50	−30	−5

In Fig 2, temper brittleness becomes apparent with cooling rates less than that of the water quench. To aid in visualizing the influence of phosphorus (and later the combined effects of phosphorus and replacement of chromium by molybdenum), it seems desirable to have a numerical value for the transition temperature. The difficulty is the definition of a transition temperature as a single temperature in the transition range. Such a definition is still a moot question among metallurgists. The most sensitive values for purposes of comparison would lie on the steepest portion of the energy curve, and, with this in mind, it appears possible to define the transition temperature arbitrarily for the data under consideration.

Inspection of Fig 2, 3, and 4 will indicate that the value of 45 ft-lb falls near the middle of the steepest portion of all the transition curves, and represents the relative placement of the transition ranges with respect to testing temperature. The transition temperatures read from the curves at 45 ft-lb are assembled in Table 3. The authors hold no brief for the value of

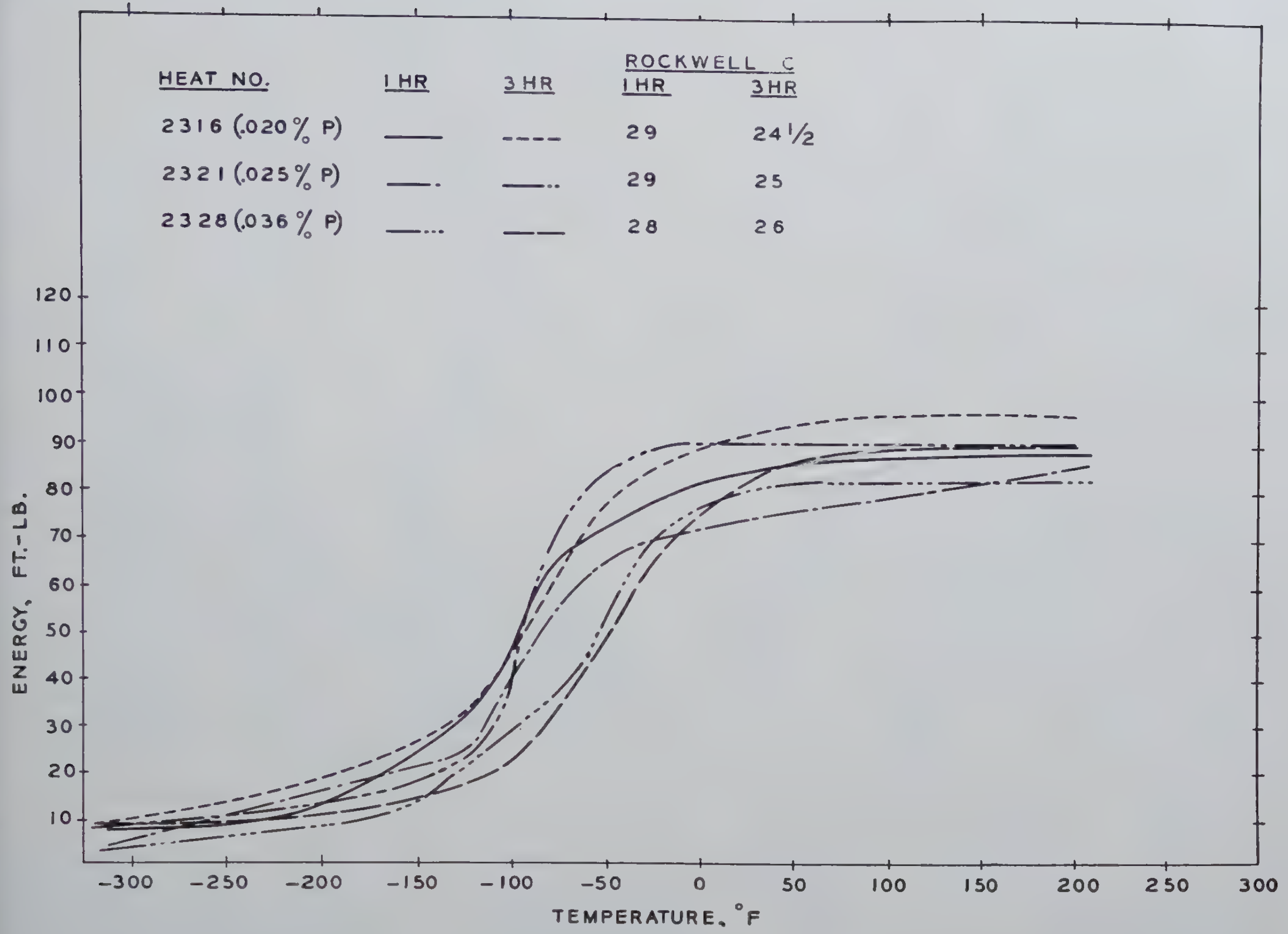

FIG 5—Comparison of transition curves of 5140 steel with variable phosphorus after one and three hours at 1150°F.
Specimens quenched in oil from 1550°F, tempered for one and three hours at 1150°F and quenched in water.

45 ft-lb except to represent this particular set of data. All of the experimental points have been shown in Fig 2, 3, and 4, so that the reader may select his own criterion, should he not agree with the authors'.

Using the transition temperatures listed in Table 3, Fig 6 was prepared to illustrate the influence of an increase in phosphorus in 5140 steel. The ordinate is transition temperature, beginning arbitrarily at —150°F. Thus the transition temperatures indicated by the upper ends of the bars are significant, but not their length. It might be thought desirable to reduce this axis to the increase in transition temperature of the embrittled as compared to the nonembrittled state. This was avoided for two reasons. It would not show the relation of transition temperature in the water quenched state to the phosphorus content. Secondly, the rise in transition temperature brought about by an embrittling treatment may be only a qualitative measure of the degree of embrittlement, unless the transition temperatures of two steels being compared are essentially the same in the nonembrittled state. At present there is no reason to suppose that the same rise in transition temperature, if it occurs in quite different temperature ranges, represents an equal change in toughness.

In Fig 6 the transition temperatures of the 0.020 and 0.025 pct P steels are essentially alike in the nonembrittled state, but show an increasing divergence as the cooling rate through the embrittling range is reduced. The divergence is small at a cooling rate of 20°F per min., but is larger with the slower cooling rates. The rise in transition temperature over the entire series of cooling rates is less for the 0.020 pct P steel than for the steel with 0.025 pct P. In the same figure, the transition temperature of the 0.036 pct P steel in the nonembrittled state is 40°F higher than that of the steels with lower phosphorus contents, but the rise in transition temperatures over the series of cooling rates is 220°F as compared to 135°F for the steel with 0.020 pct P and 170°F for the steel with 0.025 pct P. These observations indicate that phosphorus is a major cause of temper brittleness.

Effect of Phosphorus in Molybdenum-chromium Steels with Hardenability Similar to 5140 Steel

Fig 3 and 4 illustrate the extent to which the replacement of chromium by molybdenum in 5140 steel counteracts the loss in toughness caused by phosphorus.

In Fig 3 the steels have a phosphorus level of 0.021 to 0.025 pct; in Fig 4, 0.037 to 0.041 pct. With each steel the transition temperature rises progressively as the cooling rate is reduced from water quenching to ¼°F per min. Taken together with the data on 5140 steels in Fig 2, the impact transition curves of the molybdenum-chromium steels indicate that the replacement of chromium by molybdenum reduces the embrittlement caused by phosphorus to an extent dependent upon the phosphorus level and the amount of the replacement. To effect a similar reduction in embrittlement, the higher phosphorus steels require a greater addition of molybdenum than the steels with moderate phosphorus contents.

From the transition temperatures

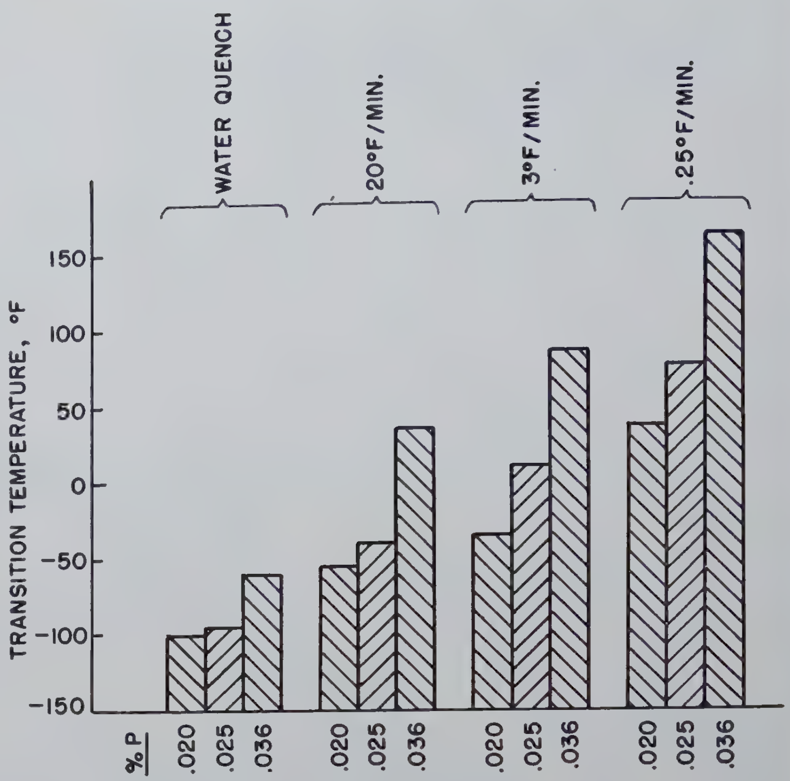

FIG 6—Effect on transition temperature of an increase of phosphorus in 5140 steel.
Transition temperatures taken from Table 3.

listed in Table 3, Fig 7 has been prepared to show the combined effects of an increase in phosphorus and the replacement by molybdenum of a part of the chromium in 5140 steel. For the purposes of this comparison, average values of the transition temperatures were taken for heats 2316 and 2321, and for heats 2336 and 2337. The trends of transition temperature with both phosphorus and molybdenum are progressive throughout the data; only the transition temperature for the water quenched specimens of the 0.11 pct Mo steel with moderate phosphorus falls out of line. In the water quenched 0.020 to 0.025 pct P series (with the exception of the 0.11 pct Mo steel) replacement of chromium by molybdenum lowers the transition temperature slightly, amounting to about a 40°F shift for 0.16 pct Mo. In the 0.036 to 0.041 pct P series, the decrease in transition temperature for the same molybdenum content is less, amounting to about a 20°F shift in transition temperature. In each steel, the transition temperature in the nonembrittled state is raised by increasing the phosphorus content from the moderate to the higher level.

Turning to the evidence for temper brittleness shown in Fig 7, temper embrittlement is minimized by molybdenum but not entirely eliminated in any of the steels under study. In general, phosphorus increases the manifestation of temper brittleness, and the replacement of chromium by molybdenum lowers the transition temperature for each phosphorus level and cooling rate under consideration. In the range of 0.020 to 0.025 pct P, the beneficial effect of molybdenum is evident at all cooling rates (except the water quenched series of the 0.11 pct Mo steel). In the 0.036 to 0.041 pct P range the difference between no molybdenum and 0.11 pct is considerable, but the difference between 0.11 and 0.16 Mo is evident only in the cooling rates of 3 and of ¼°F per min.

Discussion of Results

One effect of phosphorus is to cause a brittleness of tempered martensite which appears to be essentially the inherent brittleness of phosphorus-bearing ferrite so often noted by metallurgists. Confirmation of this was obtained in the present study of 5140 steels with 0.020, 0.025, and 0.036 pct P. The structural condition of the steel was martensite tempered for one and for three hours at 1150°F, followed by quenching in water. While the difference in tempering period had little effect on the transition temperature at each phosphorus level, a definite loss of toughness accompanied raising of the phosphorus from 0.025 to 0.036 pct. If this is caused by temper brittleness, nearly maximum temper embrittlement must have developed during the one-hour period of 1150°F. Such rapid development of temper brittleness seems improbable in view of the slow isothermal embrittlement in this temperature range shown by Pellini and Queneau for their high phosphorus steel. Thus it seems reasonable to conclude that phosphorus reduced the toughness of the tempered martensite, in the absence of temper brittleness. As deformation in tempered martensite occurs by slip in the ferrite phase, this loss of toughness is assumed to be the already well-known brittleness of phosphorus-bearing ferrite.

The inherent brittleness of phosphorus-bearing martensite described above appears to be counteracted to a slight extent by the replacement of chromium by molybdenum in 5140 steel, as illustrated by Fig 7. With the higher phosphorus level, the use of 0.11 and 0.16 pct Mo in this way lowered the transition temperature about 20°F. With the lower phosphorus level, the steel with 0.11 pct Mo appears to be out of line as mentioned earlier; however, a recession of the transition to lower temperatures may be noted in the 0, 0.04, and 0.16 pct Mo series. The use of 0.16 pct Mo lowered the transition temperatures about 40°F as compared to 5140 steel.

The data obtained in this study substantiate the evidence presented by numerous investigators that phosphorus can cause temper brittleness in tempered martensite. Temper brittleness was observed to depend on phosphorus content in 5140 steel and also to a degree in the molybdenum modifications of this grade. Using the transition temperature as a measure of the degree of embrittlement, the susceptibility to temper brittleness in the molybdenum-chromium steels decreases as more of the chromium is replaced by molybdenum.

In the 5140 grade chosen for study, it has been demonstrated that a good tolerance for phosphorus can be obtained by the use of molybdenum to replace a portion of the chromium without essential alteration of the hardenability of the steel. The desirable amount of such replacement would depend upon the phosphorus level to be expected and the tempering cycle to which the steel is to be subjected. In commercial alloy steels made by the basic open hearth or electric process, the ladle analyses for phosphorus are

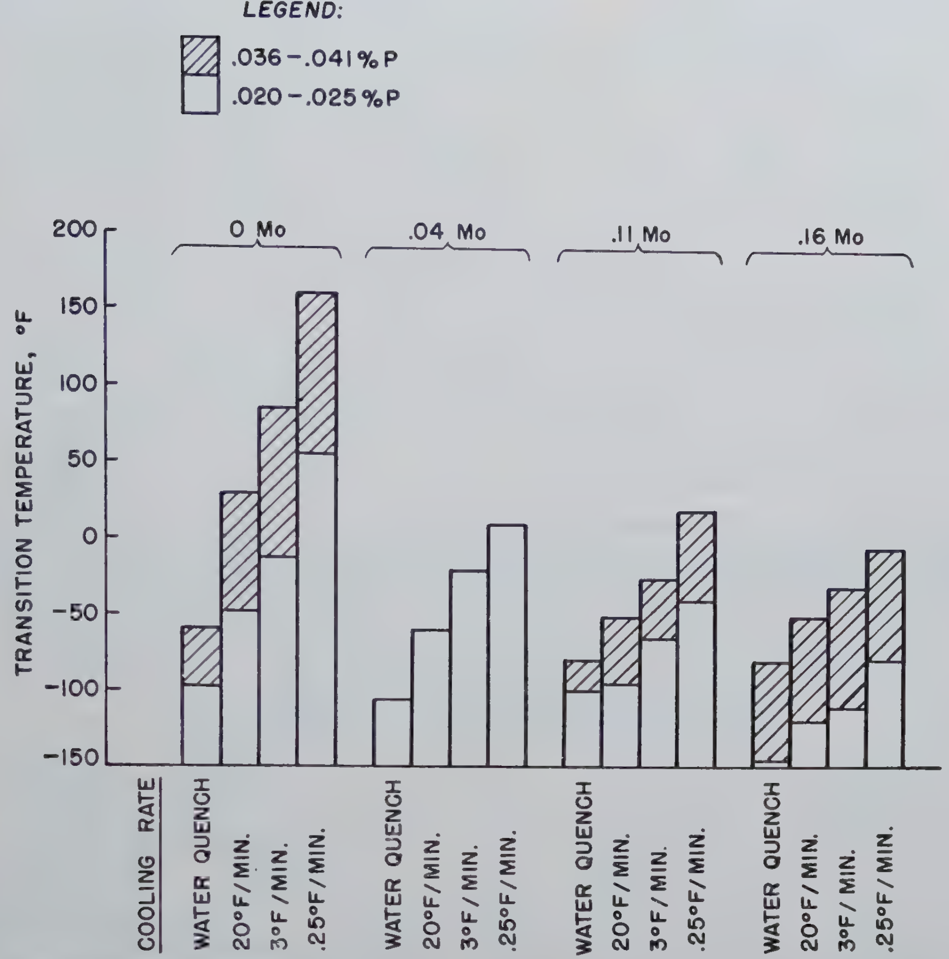

FIG 7—Combined effect on transition temperature of phosphorus and replacement by molybdenum of part of the chromium in 5140 steel. Transition temperatures taken from Table 3.

usually well below the maximum limits permitted by current AISI-SAE specifications. Because of segregation, however, substantially higher levels of phosphorus are frequently encountered, especially in material from the upper central portion of the ingots. It is in such material that the beneficial effect of replacing chromium by molybdenum would be greatest. The extent to which loss of toughness due to phosphorus segregation can be overcome is demonstrated by the 0.16 pct Mo-Cr steel with 0.041 pct P which had a lower transition temperature than the 5140 steel with 0.020 pct P when given an embrittling treatment, namely, cooling at ¼°F per min. after tempering at 1150°F.

The work reported here has dealt entirely with 5140 steel and molybdenum modifications of essentially the same hardenability. Similar work is already under way on the effect of replacing a part of the manganese by molybdenum in 1340 steel, in an effort to evaluate further possibilities in the development of steels with good tolerance for phosphorus.

Conclusions

1. Phosphorus reduces the toughness of tempered martensite even in the absence of temper brittleness. In 5140 steel this loss in toughness can be partially compensated by replacement of part of the chromium by molybdenum with no essential change in the hardenability of the steel.

2. Confirmation has been obtained of the conclusion of a number of earlier investigators that phosphorus accentuates temper embrittlement of martensite. (Structures other than tempered martensite were not included in this work.)

3. The replacement by molybdenum of part of the chromium in 5140 steel materially reduces its susceptibility to loss of toughness by temper embrittlement.

4. A study of 5140 steels and molybdenum modifications of similar hardenability has shown that replacement of part of the chromium by molybdenum can be used to improve the toughness at phosphorus levels encountered in commercial steels.

Acknowledgment

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The Effect of Quenching on the Age Hardening of Two Aluminum Alloys[*]

R. D. BARER,[†] Student Associate, and M. B. BEVER,[‡] Member AIME

Age hardening alloys are quenched from the solution treatment to room temperature in order to retain a supersaturated solid solution. Some alloys age "naturally" in this condition but in most alloys aging is induced "artificially" by heating to intermediate temperatures. Cold working of the supersaturated solid solution accelerates the aging process and quenching strains have the same effect.

The investigation reported here is a study of the progress of aging in specimens quenched directly from the solution treatment to various aging temperatures. This procedure reduces the temperature interval of quenching and the resulting quenching stresses. It also eliminates any changes which would take place in the undercooled sample at room temperature prior to aging at an elevated temperature. Isothermal aging is thus approached and its kinetics may be studied.

An aluminum-copper and an aluminum-silicon alloy were chosen for this investigation. The aging mechanism of aluminum-copper alloys is complex while the aging of aluminum-silicon alloys is nearly ideal. As standards of comparison for the samples directly quenched to the aging temperature, specimens were also age hardened by the usual procedure in which solution treated samples are first quenched to room temperature and then reheated to the aging temperature.

Review of Previous Work

The mechanism of age hardening has been the subject of a controversy which has ranged from the theory of outright precipitation of an equilibrium phase to theories based on subtle changes occurring in the matrix prior to precipitation. A detailed critical review of the literature up to 1939 is available[1] and contributions to the general theory of age hardening continue to be made.[2,3]

Age hardening, whatever its mechanism, involves the nucleation of a second phase within a supersaturated solid solution. Theoretical considerations[4,5] indicate that the rate of nucleation reaches a maximum at an intermediate temperature below the temperature at which supersaturation sets in. Studies of precipitation at various subcritical temperatures have demonstrated that the largest property changes in a given time occur at such intermediate temperatures.[6,7,8]

The precipitation of a phase from supersaturated solid solution is accelerated by strains which may result from quenching or cold work. Phillips and Brick[9] established that quenching strains are an essential condition for the age hardening of aluminum-copper alloys at room temperature, at least for aging periods of less than 30 days. They also found that on aging at 300°C the hardness increased faster and reached a higher maximum after quenching into water than after quenching directly to the aging temperatures.

Fink and Smith[10] observed preferential precipitation on slip bands and grain boundaries in aluminum-

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[†] Instructor, Dept. of Metallurgy, University of British Columbia; formerly Graduate Student, Massachusetts Institute of Technology.

[‡] Associate Professor, Dept. of Metallurgy, Massachusetts Institute of Technology.

[1] References are at the end of the paper.

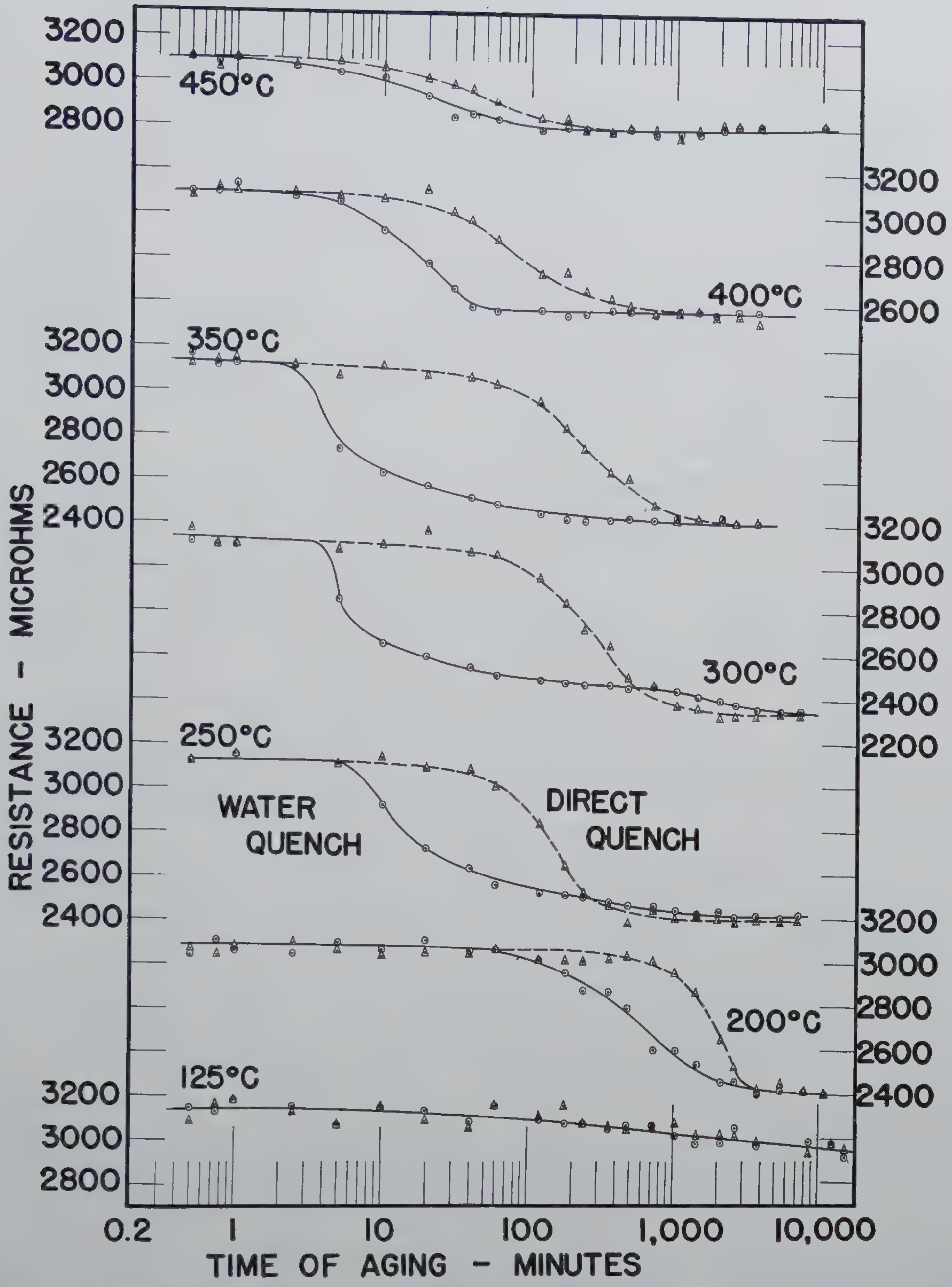

FIG 1—Electrical resistance as a function of aging time at constant aging temperatures in water quenched and directly quenched specimens of an aluminum-copper alloy.

copper alloys quenched into cold water and aged at 200°C while specimens aged after quenching into boiling water or oil at 153°C showed precipitation throughout the grains. They correlated these structural observations with hardness-time curves for various aging temperatures and concluded that the rapid hardening of specimens quenched into water resulted from accelerated precipitation in regions plastically deformed by quenching. Other investigations[11-18] have confirmed that severe quenching promotes age hardening compared to cooling at slower rates from the solution treatment.

Experimental Procedure and Results

The alloys were received as hard-rolled sheet 0.066 in. thick. They had the following compositions:

	Aluminum-copper, pct	Aluminum-silicon, pct
Cu	4.13	0.004
Si	0.002	0.97
Fe	0.003	0.005
Mg	0.001	0.001
Al (by diff.)	95.86	99.02

Specimens for hardness tests were cut from the sheet stock; they measured ½ by ⅝ in. (aluminum-copper) and ⅜ by ⅝ in. (aluminum-silicon). Specimens for electrical resistance measurements were prepared by wire drawing. The aluminum-copper wire measured 0.0392 ± 0.0002 in. in diam and the aluminum-silicon wire 0.0385 ± 0.0003 in. For heat treating, the wires were cut into equal lengths of about 3½ in.

The solution heat treating and artificial aging operations were carried out in salt or oil baths heated by electrical resistance units. The temperature was automatically controlled to ±2°C for solution treating and to ±1°C for aging. At and above 200°C a special heat treating salt mixture was used; at 125° and 70°C a light mineral oil proved suitable.

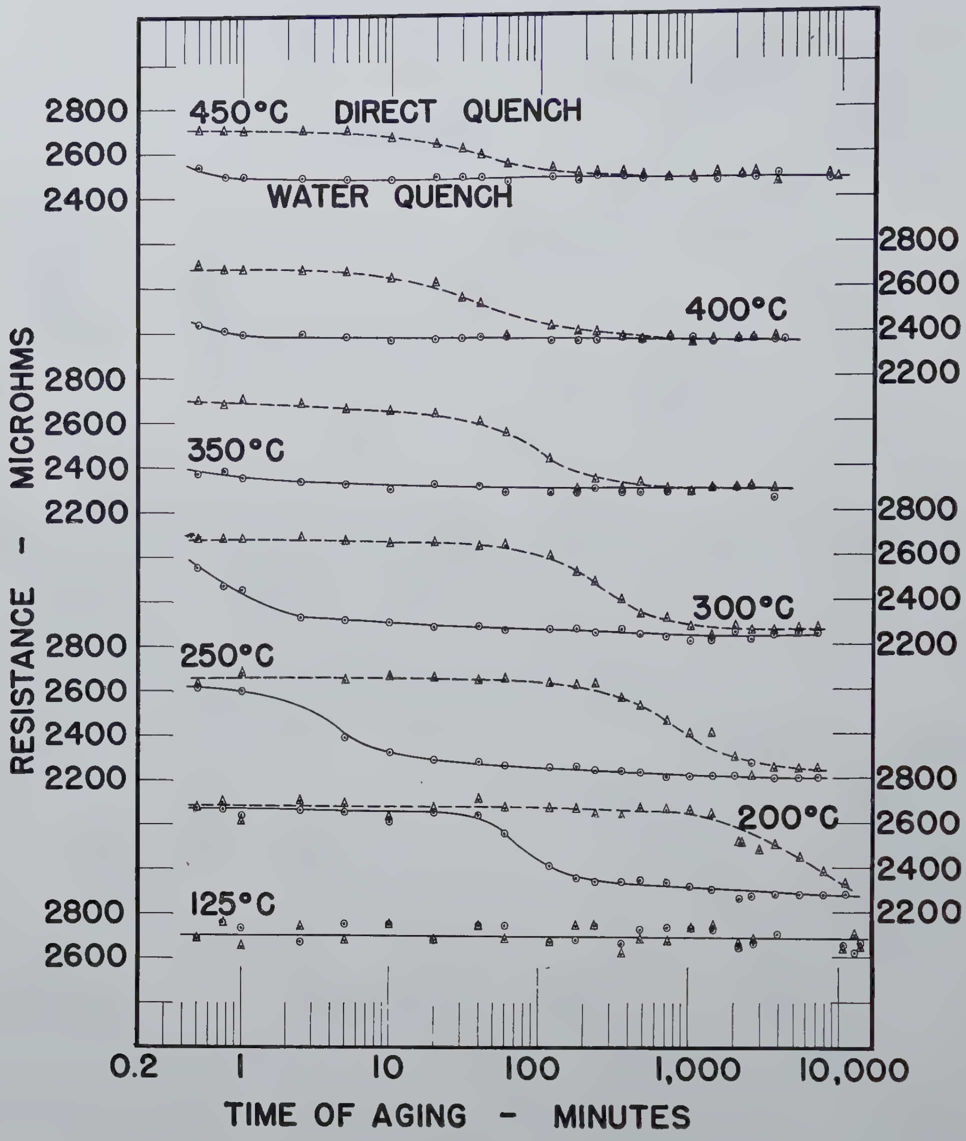

FIG 2—Electrical resistance as a function of aging time at constant aging temperatures in water quenched and directly quenched specimens of an aluminum-silicon alloy.

The solvus temperature is approximately 515°C for aluminum containing 4.13 pct copper[19] and 525°C for aluminum containing 0.97 pct silicon.[20] The aluminum-copper alloys were solution treated at 524°C and the aluminum-silicon alloys at 535°C for a period of 6 hr. In preliminary experiments the hardness of water quenched aluminum-copper samples became approximately constant after 3 to 4 hr of solution treatment at 521°C. No undissolved second phase could be found by metallographic examination. Specimens treated for 10–12 hr showed marked grain growth.

After 6 hr of solution treatment one wire and one rectangular specimen were transferred rapidly to the aging bath. These will be referred to as directly quenched specimens. Another wire and rectangular specimen were quenched in water at 20° ± 1°C and were then placed in the aging bath. The directly quenched specimens aged at 70°C were quenched into water at that temperature and transferred to an oil bath for aging. Aging treatments of less than 20 min. were timed to within a few seconds and similar precision was maintained for longer aging times. The specimens were staggered so that only one rectangular and one wire sample were ready for testing at a time.

The specimens were quenched from the aging furnace in water at 20°C. Each wire was removed from the water bath after 10–15 sec and its electrical resistance measured. The hardness was then determined on the rectangular specimen. This small delay did not appreciably affect the hardness. For specimens aged less than 5 min., the schedule was modified so as to allow almost immediate determination of resistance and hardness.

Electrical resistances were measured on a Kelvin double bridge using an effective specimen length of 2.376 in. The resistances were determined in microhms and are so reported here. Care was exercised not to deform or mar the wires, and any variations in tension applied by the holder were negligibly small.

The Rockwell F scale could be used with good reproducibility on the aluminum-copper samples, but was unsatisfactory for the aluminum-silicon alloys. All hardness values were therefore determined by superficial hardness tester on the Rockwell 15-T scale. Hardness readings on the same specimen of aluminum-copper alloy agreed within two or three points, but the

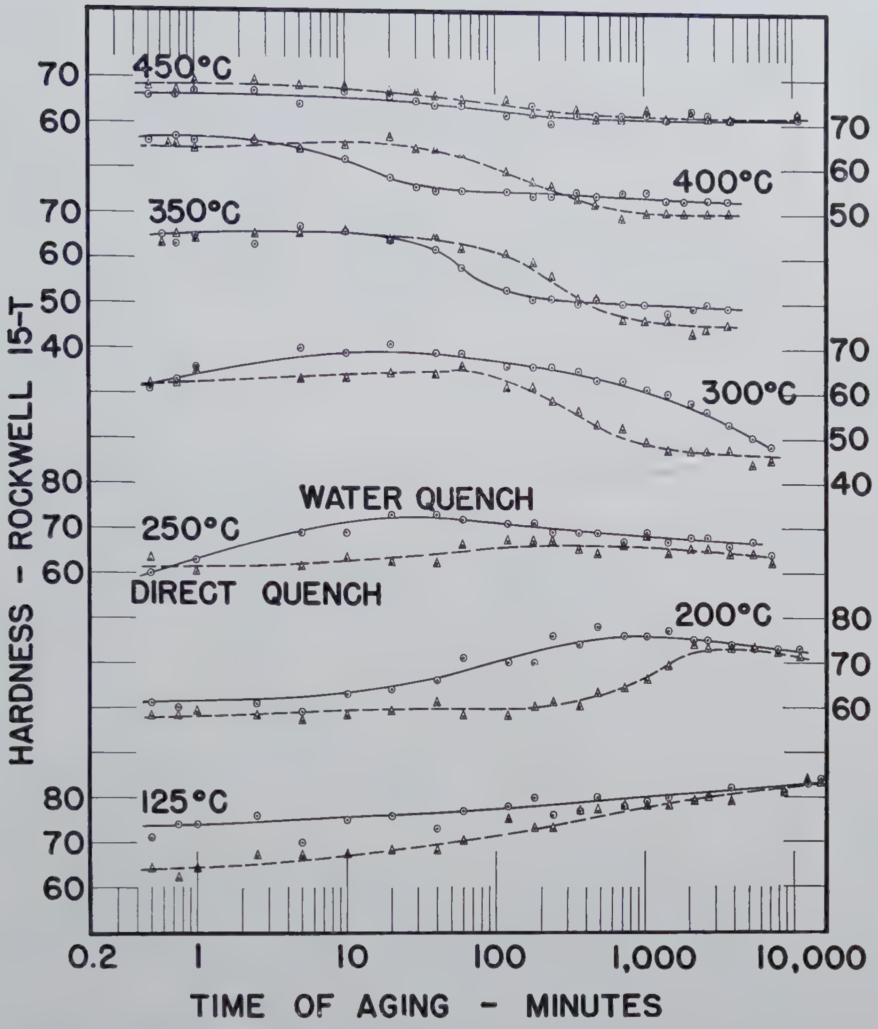

FIG 3—Hardness as a function of aging time at constant aging temperatures in water quenched and directly quenched specimens of an aluminum-copper alloy.

spread obtained with the aluminum-silicon specimens was large. Five, and occasionally six, separate readings were taken on each specimen in a standardized geometrical pattern. Only the averages of these readings are reported.

Both alloys were aged at 70, 125, 200, 250, 300, 350, 400 and 450°C. Fig 1–5 report all observed values graphically.

Discussion of Results

SOURCES OF ERROR

Measurements of hardness and resistance were made at room temperature on separate samples for each aging temperature and time. Aside from experimental advantages, this procedure made it possible to compare all data directly without reducing them to a common temperature. It should be kept in mind that each point plotted in Fig. 1–5 represents a different specimen.

The data obtained for aging temperatures above 300°C fit simple curves well. The observed values become less regular for aging below 300°C and are somewhat erratic at 125° and 70°C.

The resistance and hardness of samples in the water-quenched condition before aging were also determined. While the hardness values showed good agreement, the resistance values were spread over a considerable range, probably owing in large measure to variations in the quenching action. It is known[18,21] that the quenching rate affects the properties of aluminum alloys in the water quenched condition much more than after aging.

GENERAL FEATURES OF AGING CURVES

The aging curves (Fig 1–5) show the effects of aging temperature, type of quench and alloy composition on the aging process. Before discussing these factors individually, some general features of the curves will be considered. The first statement is general; the comments under (2) to (5) refer only to aging at 200°C and above, while the curves for 70° and 125°C are discussed under (6) and (7).

1. The changes in hardness and in electrical resistance are not directly comparable even for the same time and temperature of aging. Aside from the different nature of hardness and electrical resistance, in this investigation the two properties were measured on specimens of different size and shape. The resulting different quenching strains complicate any comparison by an additional variable.

2. The electrical resistance reaches steady values after sufficiently long aging. These values vary with the aging temperature, but are nearly equal at any temperature for water quenched and directly quenched samples. This applies to both alloys.

3. The resistance of the aluminum-copper alloy decreases sooner after a water quench than after a direct quench. At 250° and 300°C the de-

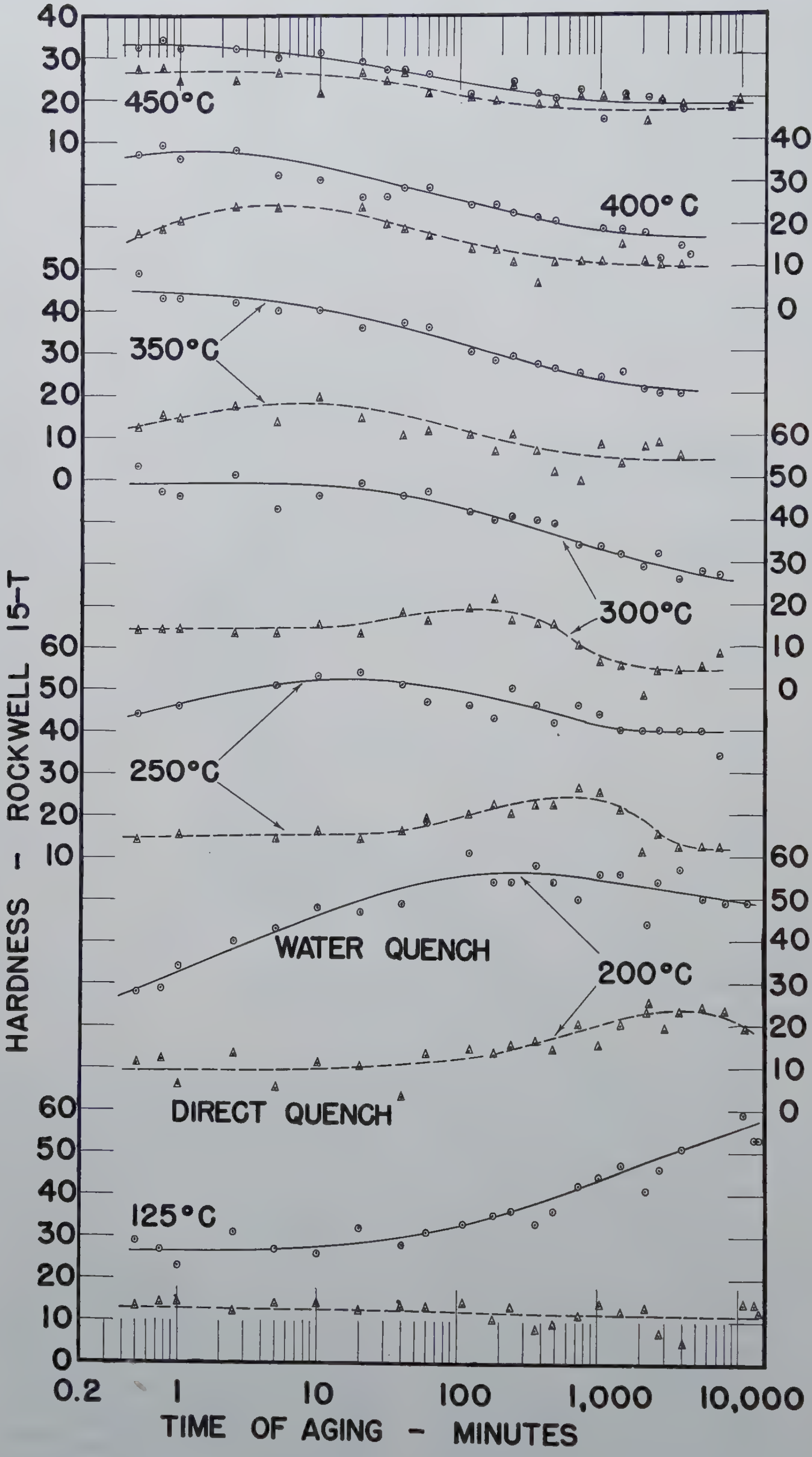

FIG 4—Hardness as a function of aging time at constant aging temperatures in water quenched and directly quenched specimens of an aluminum-silicon alloy.

crease in resistance slows down more in the water quenched than in the directly quenched specimens toward the end of the aging period so that the curves cross.

4. The resistance of water-quenched aluminum-silicon alloys decreases very rapidly at temperatures above about 250°C; a large fraction of the total decrease occurs in the first minute of aging. The decrease in resistance of directly quenched aluminum-silicon alloys begins slowly and requires considerable time for its completion.

5. The alloys harden more rapidly after a water quench than after a direct quench. The maximum hardness of the water quenched specimens exceeds that of the directly quenched specimens in most cases. The difference in the rate of hardening and in the maximum hardness reached tends to be larger in the aluminum-silicon than in the aluminum-copper system.

6. The difference in quenching interval between water quenching and direct quenching decreases as the aging temperature is lowered, but even at 70°C the two quenching treatments do not lead to identical results in all respects. Regardless of the type of quench the resistance of aluminum-copper alloys aged at 125° and 70°C decreases slowly, possibly after a small initial rise. During the aging times used the resistance of the aluminum-silicon alloys undergoes no change as the result of aging at 125° and 70°C.

7. The hardness of aluminum-copper alloys increases slowly with aging at 125° and 70°C. At the latter temperature the directly quenched samples lead by a small margin over the water quenched samples. This fact is consistent with the observation of Gayler[16] who found that quenching into boiling water promoted the age hardening at 130°C of an aluminum alloy containing 4 pct copper more effectively than quenching into cold water. The behavior of the hardness of the aluminum-silicon alloys aged at 125° and 70°C is particularly interesting; the directly quenched samples show no change during the longest periods of aging employed while the water quenched samples increase steadily in hardness.

THE EFFECT OF AGING TEMPERATURE

Fig 6 and 7 show the total changes in resistance of the aluminum-silicon alloys against the aging temperature for different times. The plotted points are taken from the curves in Fig 2 and 5. Resistance-temperature curves for aluminum-copper alloys show the same pattern as the aluminum-silicon alloys although in a less pronounced manner. For each aging period the decrease in resistance reaches a maximum at some intermediate temperature. As the aging period is lengthened the maxima become more marked. They also shift to lower temperatures because the depletion of solute from the solid solution causes the reaction to reach a maximum at lower temperatures where a sufficient degree of supersaturation can be expected.

The hardness-temperature curves were simple only for water-quenched aluminum-silicon alloys (Fig 8). The

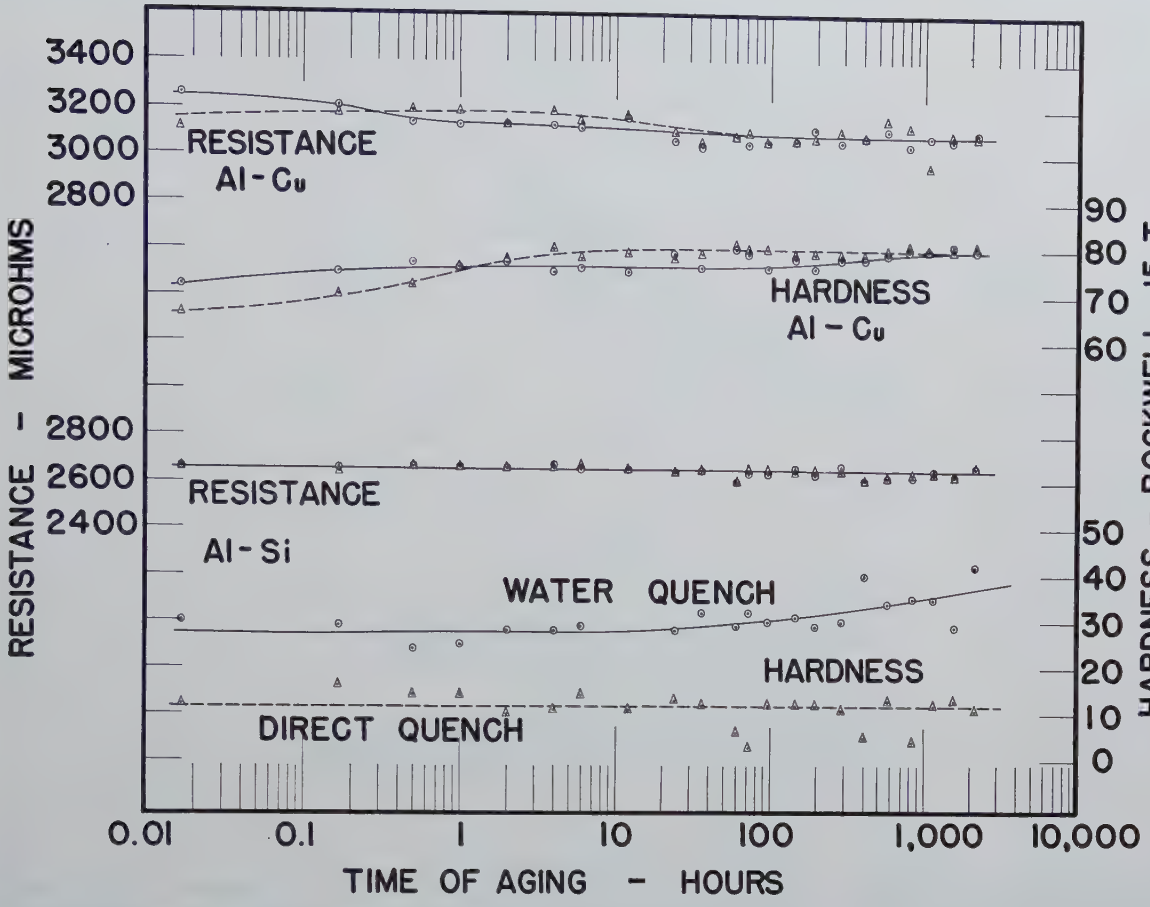

FIG 5—Electrical resistance and hardness as functions of aging time in water quenched and directly quenched specimens of an aluminum-copper alloy and an aluminum-silicon alloy aged at 70°C.

hardness peak was attained at lower temperatures as the aging period was lengthened. Hardness curves for aluminum-copper and directly quenched aluminum-silicon alloys did not show such a simple pattern.

Chevenard, Portevin and Waché[8] found a maximum hardness value at 200°C for a water-quenched aluminum alloy containing 0.63 pct silicon and 0.13 pct iron aged 8 hr. This value is in good agreement with the corresponding result of the present investigation. In experiments of Jetter and Mehl[14] with aluminum-silicon alloys a maximum of initial dilation against temperature of aging seemed to be approached at 236°C which was the upper temperature limit of their observations.

The temperatures for maximum total change in resistance (Fig 6 and 7) are not necessarily identical with the temperatures for maximum rates of resistance changes. In fact there is no satisfactory method of defining these rates in a manner which would allow an absolute comparison between different aging temperatures. The terminal solubility of copper and silicon in aluminum increases with temperature and the resulting resistance of the saturated solution increases also. The change in resistance is therefore smaller the higher the aging temperatures.

A comparison on the basis of the completion of a specified fraction of the aging reaction is not a comparison in absolute terms. It implies that the aging curves have or should have similar shapes. For complex reactions in the solid state this assumption is not warranted. Nevertheless such arbitrary measures of the rate as the time required for half the total reaction are of some value and have been used for finding activation energies.

ACTIVATION ENERGIES

The rate of the aging process may be expressed by the equation

$$r = c \exp - \frac{Q}{RT}$$

In this equation the reaction rate r must be measured by some arbitrary standard such as the reciprocal of the time required for one-half of the total change in resistance or the reciprocal of the time required to reach maximum hardness. Q is the activation energy for the over-all process, T is the temperature and R and c are constants.

The activation energy may be found from a plot of the logarithm of the rate against the reciprocal of the absolute temperature. Such curves were straight in the temperature range of 200–250°C, and in some instances up to 300°C. At higher temperatures some of the curves became erratic, but in most cases they bent back toward the abscissa. This behavior is to be expected from the eventual reversal of the aging rate with increasing temperature.

The activation energies determined from the straight portions of the curves are listed in Table 1. In every instance the activation energy was larger for the water-quenched than the directly quenched alloy. The faster aging rate of the water-quenched samples therefore must have been due to differences in the value of the factor c.

Guy, Barrett and Mehl[17] found that the activation energy for precipitation in the copper-beryllium system is less than the activation energy for diffusion of beryllium in copper. A similar relation had been noted by Jetter and Mehl[14] in their investigation of alu-

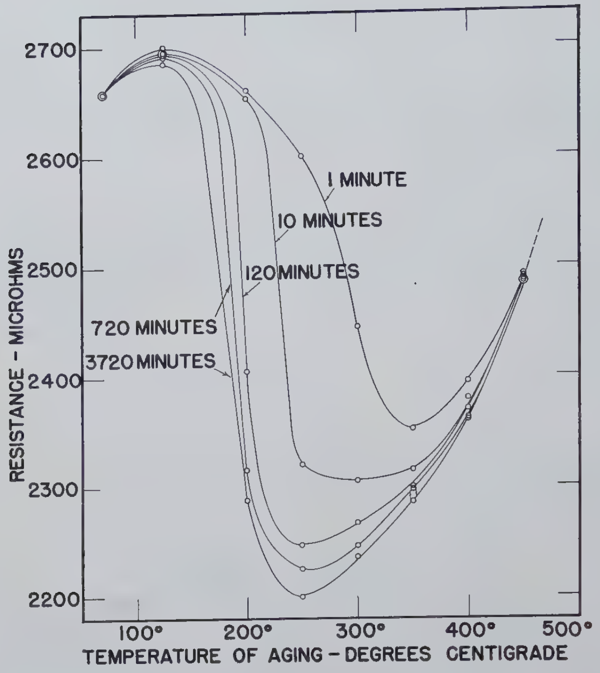

FIG 6—Electrical resistance of water quenched specimens of an aluminum-silicon alloy as a function of temperature at constant aging times.

Table 1 . . . Activation Energies (in Calories)

Alloy	Based on Resistance		Based on Hardness	
	Water Quench	Direct Quench	Water Quench	Direct Quench
Aluminum-copper.....	30,500	24,100	34,200	25,100
Aluminum-silicon......	24,300	15,900	24,100	22,900

minum-silicon alloys. In the investigation reported here this relation between activation energies of diffusion and of aging was confirmed.

THE EFFECT OF QUENCHING

As stated in the description of experimental procedure, the directly quenched samples aged at 70° and 125°C were quenched into media which were different from those used with all other directly quenched specimens. While the latter were transferred from the solution bath into the salt bath and remained there for aging, the specimens aged at 125°C were quenched into a bath of oil in which they were aged and the specimens aged at 70°C were quenched into water at that temperature and aged in oil. This difference in quenching procedure is one reason why the quenching stresses cannot be considered as continuous or simple functions of the aging temperature. The sequence of molten salt (200°C and over), oil (125°C) and water (70°C), however, parallels the increase in quenching severity resulting from the decrease in temperature. A correlation of all runs on the basis of decreasing temperature is therefore reasonable.

While the final values of the resistance of water quenched and directly quenched samples are alike for any aging temperature, the rates at which these values are approached are generally more rapid after water quenching than after quenching directly to the aging temperature. This accelerating action of water quenching is particularly pronounced in the medium temperature range of aging. The water quench also accelerates the rate of hardening and with some minor exceptions raises the maximum hardness obtainable.

The accelerating effect of the water quench may be owing to one or both of two causes. In the first place, the number of available nuclei is larger at room temperature than at elevated temperatures according to Becker's analysis of nucleation.[4] This is a simple effect of temperature. Secondly, rapid cooling by quenching into water produces thermal stresses and the resulting strains create favorable regions for the progress of age hardening. This effect results from the rapid change in temperature.

The number of nuclei is larger at room temperature than at elevated aging temperatures because the critical radius for a stable nucleus decreases as the temperature is decreased. The greater undercooling and the greater degree of supersaturation with a receding solvus cooperate toward this decrease in critical nucleus size. In order to be effective in subsequent aging at elevated temperatures, however, the nuclei must remain in existence. They must, therefore, grow at room temperature or during heating so that they will not be below the critical size characteristic of the higher temperature.

If it is assumed that even a fraction of the nuclei existing at room temperature survives on heating, a difficulty arises from the generally accepted explanation of the phenomenon of retrogression or restoration. According to this explanation the property changes of an alloy aged at room temperature revert partially in the direction of the unaged state because on heating active aggregates go again into solution. Since the nuclei resulting from a short period at room temperature are smaller than the aggregates resulting from long-time aging at this temperature, they can be expected to resist the effects of higher temperature less strongly.

A difference exists between room-temperature age hardening and room-temperature nucleation: the matrix surrounding the hardening aggregates

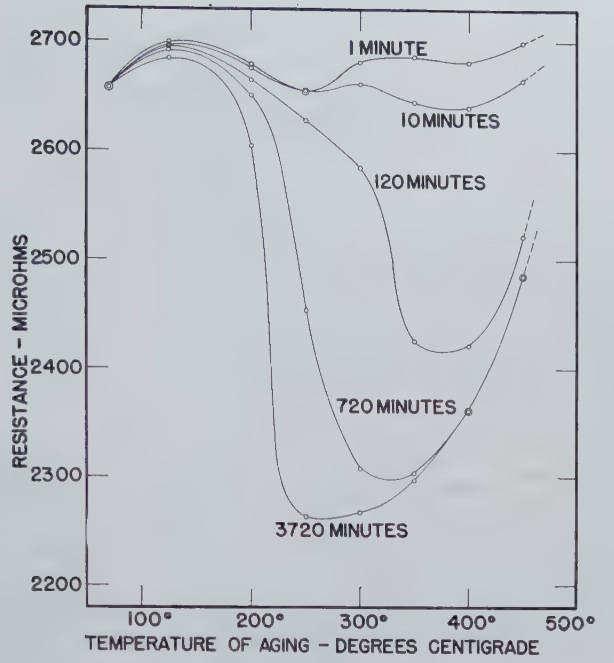

FIG 7—Electrical resistance of directly quenched specimens of an aluminum-silicon alloy as a function of temperature at constant aging times.

approaches closer to the equilibrium state than does the matrix which surrounds the nuclei existing at room-temperature. The supersaturated matrix may have a stabilizing effect on the nuclei which is absent in the matrix after aging. Whether such a stabilizing effect is sufficiently strong to protect small nuclei at a temperature where retrogression would occur is open to question. It can be stated with certainty only that the effect of room temperature on nucleation favors the aging of quenched alloys to whatever extent nuclei survive upon reheating.

An alternative or additional explanation of the acceleration of aging caused by water quenching is based on the effect of strains on the age hardening process. Plastically deformed regions are regions of instability. Their high energy favors any rearrangement which tends toward a more stable condition. In addition to explaining the increase in the rate of aging, strains can also explain the greater total hardness obtained by water quenching than by direct quenching. Following an argument of Fink and Smith,[10] the increase in hardness results from the presence of zones of preferential aging throughout the grains; the spread in time between aging at the grain boundaries and in the bodies of the grains is thus reduced and this causes a more concentrated aging effect and greater hardness. It should be emphasized, however, that a corresponding argument can be based on the nucleation effect of low temperatures.

It may be argued that the effects of strains are removed on reheating to elevated aging temperatures. Hartnagel[12] concluded from his work that relief of quenching stresses takes place and this is also to be expected from the work of Kempf and Van Horn[22] on residual stresses in aluminum alloys. Regardless of the relief of residual stresses during aging, the plastic strains due to the thermal shock of quenching create regions of instability in which the aging process takes place preferentially. In fact, the process by which the effects of plastic deformation are relieved in age hardening is probably closely related to the aging process.

THE EFFECT OF ALLOY COMPOSITION

When the aging curves of the two alloys are compared, several differences become apparent. Except for aging at 125° and 70°C, the electrical resistance of water quenched aluminum-silicon specimens decreases more rapidly than that of the water quenched aluminum-copper specimens. The rates of hardening behave correspondingly, although to a less marked degree. At the two lowest aging temperatures the water quenched aluminum-silicon alloy aged less rapidly than the aluminum-copper alloy, especially when considered in terms of the first appreciable aging effect.

The directly quenched samples of both alloys changed in resistance and in hardness at comparable rates at most temperatures but the directly quenched aluminum-silicon alloys showed almost no effect of aging at 125° and 70°C.

With minor exceptions the accelerating effect of water quenching is thus more marked for the aluminum-silicon than for the aluminum-copper alloy. This observation must be interpreted in the light of the fact that the age hardening mechanism is simpler in the aluminum-silicon than in the aluminum-copper system.

Summary and Conclusions

Two alloys of aluminum were aged at various temperatures after quenching from the solution treatment directly to the aging temperatures and also after first quenching into water. The progress of the aging reaction was followed by electrical resistance and by hardness measurements.

The absolute amount of change in electrical resistance as a function of the aging temperature went through a maximum. This was true for both

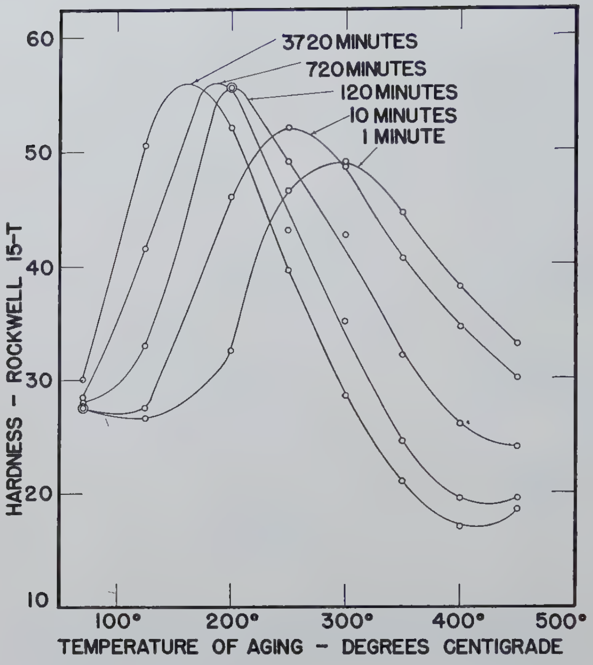

FIG 8—Hardness of water quenched specimens of an aluminum-silicon alloy as a function of temperature at constant aging times.

alloys and regardless of the type of quench, given a certain minimum time of aging. The change of hardness behaved similarly although some of the curves were of complicated shape. It may also be concluded that the age hardening rates went through maxima at intermediate temperatures, although no absolute basis exists for comparing these rates at different temperatures.

At most temperatures water quenching greatly accelerated the rate of aging compared to directly quenched samples. This accelerating effect is the result of strains caused by the thermal shock of quenching assisted to an unknown extent by the effect which exposure to room temperature has on nucleation.

At most temperatures the water-quenched aluminum-silicon alloy aged more rapidly than the aluminum-copper alloy, while the directly quenched alloys aged at comparable rates. At the two lowest aging temperatures, however, the water quenched aluminum-silicon alloy aged less rapidly than the aluminum-copper alloy and the directly quenched aluminum-silicon alloy showed almost no effect of aging. At most temperatures, the accelerating effect of water quenching over direct quenching is larger for aluminum-silicon than for aluminum-copper alloys.

Acknowledgments

The authors gratefully acknowledge the help received from several staff members of the Department of Metallurgy at the Massachusetts Institute of Technology. They desire especially to record their indebtedness to Professor Morris Cohen. Thanks are also due to the Aluminum Company of America for furnishing the high-purity alloys used in this investigation.

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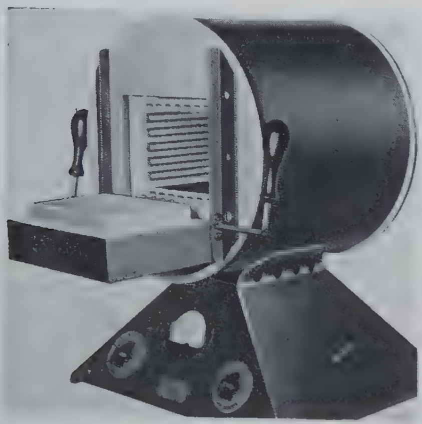
AMONG THE MANUFACTURERS:

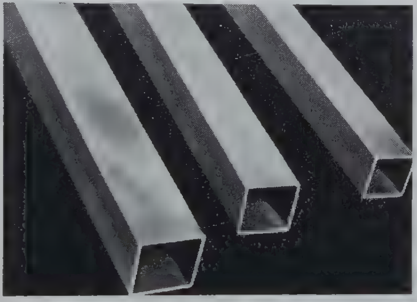
Laboratory Furnaces

New laboratory furnaces have been designed for general requirements, such as drying of precipitates, ash determinations, fusions, ignitions, heating metals and alloys, enameling and ceramic firing, heat treating and for general experimental work. Made by Hevi Duty Electric Co., Milwaukee 1, they depart from the usual rectangle shape, this furnace being housed in a cylindrical shell mounted on a pyramidal base, allowing free circulation of air and eliminating trapped heat in the base. Instruments and controls remain at practically room temperature; improved insulation design cuts radiation loss; there are 36 steps of control through a tap-changing transformer: the recessed position of the controls affords full protection; moreover, the instruments are easily accessible through removable panels.



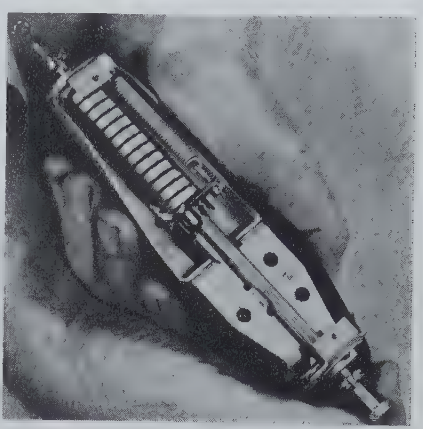
Tubing in Unusual Shapes

Electricweld tubing in unusual shapes for streamlined modern design, and in square, rectangular and oval shapes, is now being produced by Jones & Laughlin Steel Corp. Such tubing is used both for eye-appeal and for structural advantages. The square tubing, shown in the photograph, is of minimum size of $\frac{3}{8}$ in. and maximum of 3 in., with Nos. 14 to 20 gauge wall. Other shapes can be produced to customers' specifications within reasonable size limits.



Force Indicator

A new force indicator for designers and engineers has been introduced by the Hunter Spring Co., Lansdale, Pa. It is to be used for making force measurements for spring specifications and the like. It utilizes a precision compensated spring system to give easy force measurements, accurate to $\frac{1}{2}$ graduation or $\frac{1}{2}$ of 1% at full scale of the dial indicator. The spring system is composed of the main compression spring, the compensating extension spring and the load-transmission rod-centering springs and the springs internal to the dial indicator. Accuracy depends on the relationship between force and spring displacement, linear throughout the dial range; the gradient of the spring system which is made with an accuracy of 1/5 of 1% and the lack of friction, which is virtually eliminated. The currently-available unit has a 10 lb. capacity.



Manufacturers' Publications

An elaborate booklet on furnaces for melting and refining iron, steel, nickel and copper has been published by the Pittsburgh Lectromelt Furnace Corp., Pittsburgh, called Catalog No. 7. It is profusely illustrated with photos and diagrams and presents tables of dimensions of various furnace parts.

Wheelco Instruments Co., Harrison and Peoria Sts., Chicago 7, presents a 4-page pamphlet giving case histories where the Wheelco controls are used.

Brown pH and conductivity recorders and controllers are set forth in Catalog 15-12 of the Brown Instrument Co., Philadelphia 44. Case histories are given from several industries, including electroplating with nickel baths.

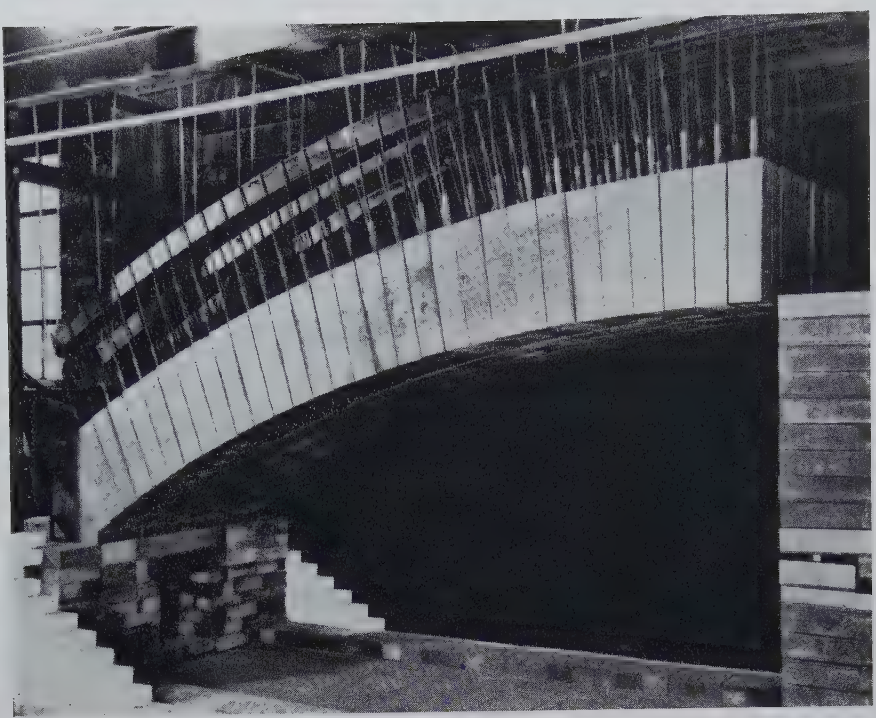
Lithium as a deoxidizer is portrayed in a 4-page pamphlet issued by Metalloy Corp., Rand Tower, Minneapolis 2, this pamphlet dealing with lithium for the treatment of high conductivity copper and copper-base alloys.

A booklet on magnesium in die castings has been published by Doehler-Jarvis Corp., 386 Fourth Ave. New York 16. It portrays some applications of such castings and lists some of the inherent advantages of magnesium for the purpose.

Men of Industry

Dr. Roy D. Hall, formerly with the Westinghouse Electric Corp., was the fifth recipient of the medal awarded annually by Stevens Institute of Technology for outstanding achievement in powder metallurgy. Stevens is the first college in the United States to establish a chair of powder metallurgy.

Christopher Williams, formerly with the Mesta Machine Co. and Mechanical Handling Systems for several years, has formed a new engineering firm, Christopher Williams & Co., Inc., 923 Penn Ave., Pittsburgh. The company will design and build rolling mill equipment, and handle other lines.



Interior view of partially constructed new type of basic roof.

General Refractories Opens New Baltimore Laboratory

On June 27 the General Refractories Co. officially opened their new Baltimore laboratory. It was a privilege to be present at the opening ceremonies and to visit the new laboratory and their Baltimore refractories plant. Refractory brick made of magnesite, or chromite or mixtures of these two base materials are produced at this plant, as are both fired and unfired, plain and steel clad (Steelklad) brick. Production of basic brick has been considerably increased by the development of the basic roof and the all-basic open hearth furnaces.

The new laboratory includes a pilot plant completely equipped, both to study manufacturing processes and to produce new products for experimental purposes. Equipment for crushing and grinding, screening and mixing, including mixing under vacuum or with steam jacket heating, prepares standard or experimental mixtures for testing. Either an extrusion unit for molding materials into stiff mud brick shapes or a hydraulic press to form the brick shapes is available.

The magnesium oxide used in the magnesite bricks or mixtures including magnesium oxide is produced from sea water. Magnesium present as salts in the sea water is precipitated as magnesium hydroxide by calcium oxide from burned dolomite. The magnesium oxide in the burned dolomite is recovered along with the magnesium hydroxide from the sea water. This was an interesting and economical application of elementary chemistry.

Another basic principle used in making brick was to combine some large and some fine particles to obtain the maximum density of finished product, but an intriguing application of this principle is used. Chrome bricks swell when the iron oxide present in the furnace combines with the brick. Magnesite bricks shrink when heated. A mixture of 60 per cent coarse chrome ore and 40 per cent fine magnesium oxide combines the high density obtained from using varied sizes with a compromise mixture to minimize changes in dimensions when heated in the open hearth furnaces. These brick are dried but not fired and can be used simply as standard refractory brick or are made with steel plates on some surfaces. The steel plate oxidizes and bonds well to the adjacent brick at the temperatures used.

Laboratory facilities for all types of testing of refractory bricks are available. It was not surprising to see equipment for various ASTM tests available such as heating and cooling for spalling and for shrinkage, hot load tests and others. Nor was it unexpected that a fine chemical laboratory for checking and controlling composition would be available. It was remarkable to find the research facilities that were available in this refractories laboratory. A spectograph, metallurgical microscopes, petrographic microscopes, a dilatometer, and even quite elaborate facilities for X-Ray diffraction studies were present. Fundamental research on refractories should soon be making itself felt as a result of the work of this laboratory.

Report on Cuban Nickel

The Cuban nickel deposits, while accessible and reasonably economical to operate, are not competitive with Canadian ores, since the latter contain many commercial by-products such as copper, platinum, gold and silver, not found in the Cuban ores. This is one of the conclusions of a recent report by the Office of Technical Services, U. S. Department of Commerce, on the Nicaro Nickel Project in Cuba. The report concludes that the nickel furnished during the war was of great importance in relieving shortages of this critical metal and it is "regrettable" that the project was not kept in at least a stand-by condition "as an insurance against future emergencies."

The project turned out 63,500,000 lbs. of nickel, chiefly in oxide form. Invested in the enterprise was $32,000,000 by the Defense Plant Corp. for construction and $20,000,000 by the Metals Reserve Corp. for operation. A novel reduction process, pioneered by the Freeport Sulphur Co., was utilized. Nickel and cobalt were precipitated after reaction of the ore with producer gas and oil combustion products in Herreshoff furnaces. The resulting pure nickel was acceptable for production of steel and alloys and an attempt to produce ingot nickel was abandoned.

A complete report is available at $20 per copy in photostat and $6 in microfilm, by ordering PB 97271, Review of the Nicaro Nickel Project from the Library of Congress, Photoduplication Service, Publication Board Project, Washington 25, D. C., accompanied by check or money order, payable to the Librarian of Congress.

The deadline for Annual Meeting papers will be Oct. 15, 1949.

Book Reviews

Practical Considerations In Die Casting Design

Published by New Jersey Zinc Co. in 1948, 246 pages, $3.00.

Reviewed by F. R. Morral

This is a sequel to a previous book published on the subject of die casting, particularly to designing for die casting, in 1946. This new book is attractively printed with over 220 figures of die cast parts, especially of zinc alloys.

A chapter on general considerations in the design of die castings calls attention to the part, its sizes, alloys to be used, ease of machining, dies and cost. Practical points considered (which are the aim of this book) are section thickness, cores, when to use and when to avoid undercuts, the proper use of fillets and edges, die cast threads and inserts, adding utility to die castings by taking advantage of intricacies, cores, coatings, ribs, fins, beads, and bosses, and fastening expedients. The die casting of wheels, gears, and cams, and the possibilities of piercing and forming are also discussed. How design affects flash removal costs and polishing cost as well as appearance factors including decorative features and lettering are subjects for individual chapters.

The anonymous author points out that there is extensive literature on the subject, and on a page of bibliography 10 books are listed. Some of this literature gives specific rules of proceedure; but it is advised to seek help from experienced die casters to minimize the penalties of inexperience. An 8-page double column index completes this attractive book on zinc die castings.

Hydrogen in Metals

Donald P. Smith. University of Chicago Press. 1948. 366 pp. $10.00.

Reviewed by Michael B. Bever

This monograph deals with the occlusion (absorption and retention) of hydrogen by massive solid metals. The effects of hydrogen on the engineering properties of industrial metals and the solution of hydrogen in liquid metals are considered only in supplementary notes and the bibliography.

This work is exceedingly well documented in a bibliography of nearly 1500 entries. Much of the text is devoted to critical abstracts of the literature supplemented by tables and graphs. This evidence demonstrates that important variables other than pressure and temperature affect the rates and amounts of hydrogen occlusion. Among these variables are structural conditions resulting from electrodeposition and plastic deformation as well as the thermal history of the metal and previous gas occlusion. In addition to absorption from the gas phase Dr. Smith discusses the occlusion of hydrogen originating in aqueous solutions. Throughout the book acclusion is correlated with other phenomena such as electrical and magnetic behavior and x-ray diffraction.

The author states that the view presented by him "is confined to the experimental observations and such deductions as seem directly to follow." Such caution, while desirable where data are inadequate, imposes a serious limitation and aggravates the tendency toward isolation which is a potential shortcoming of any monograph. There may also be considerable variance of opinion as to what deductions follow directly from observations. In the author's view the hypothesis of rift occlusion qualifies in this respect but the reviewer would only concede that Dr Smith has argued this case persuasively. The most obvious weakness of the rift hypothesis is the fact that it has remained entirely qualitative.

The author's emphasis on the roles of structure and of strain merits unreserved approval. One may also confidently share his conviction that the phenomena of hydrogen occlusion hold important clues on the nature of the occluding metal. Primarily, however, Dr. Smith's work will be of lasting value as a source of references and data on the physical chemistry of metal-hydrogen systems.

Surface Active Agents

Anthony M. Schwartz and J. W. Perry, Interscience Publishers, Inc., 579 *Pages,* $10.

This book is an attempt to summarize the achievements of the last three decades in developing a host of new surface active agents. Different types of products are reviewed with particular attention to their laboratory synthesis, commercial production, and characteristic properties. Attention has been directed to practical applications of surface active agents and to the utilitarian effects—foaming, wetting, detergency, emulsification, spreading, etc. Fundamentals of the chemistry and physics of surface phenomena have been summarized. The book is designed to appeal to practicing chemists in general, to advanced students in chemistry and chemical technology and to specialists in the production, investigation, and application of these agents. References are made to the techniques in the metal, textile, leather and other industrial fields.

Mechanical Testing of Metals and Alloys

By P. F. Foster. 4th ed. Sir Isaac Pitman & Sons, Ltd., London, 1948. 319 p., illus., diagrs., charts, tables, cloth, 18s.

Modern testing equipment and methods are described in detail following a discussion of the elementary theory of elasticity and the structure of metals. The book also deals in a practical way with the fundamentals of present-day developments in metals testing. The last chapter describes certain test phenomena and explains the meaning of the characteristic results. A group of tables of properties of metals and alloys is appended.

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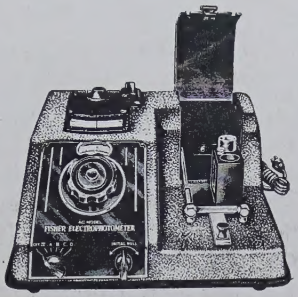

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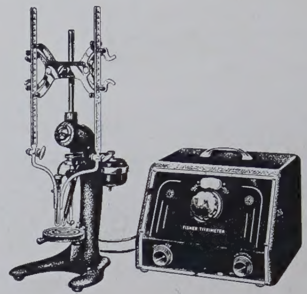

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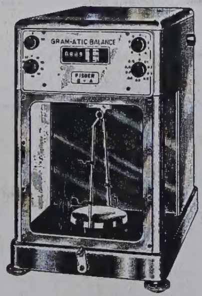

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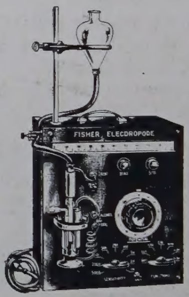

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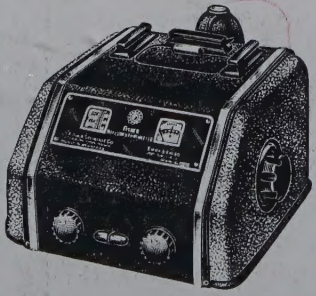

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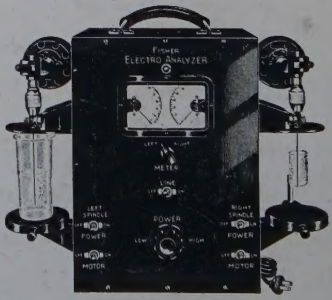

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